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ABSTRACT

French Vertical Flow Constructed Wetlands (French VFCWs) are widely used for the treatment of wastewaters from small communities. In the system, unsettled wastewater is percolated through two successive stages of filter-cells planted with reeds. This causes the formation of a surface sludge layer. This layer plays positive roles in the treatment performance, but also leads to clogging. The objective of this study was to contribute to the description of the sludge deposits characteristics and their dynamics of evolution which may control the development of clogging. Representative samples of sludge deposits were taken from fourteen French VFCWs full-scale plants and analyzed for particle size, dynamic vapor sorption and other parameters of composition to compare their structure and evaluate the factors of influence. Results showed that ageing of the surface deposits layer over the years of operation in each plant induced the formation and integration of microaggregates within the initial macrostructure of fresh organic matter. The humification process of the organic matter was found to play a key role in the aggregation process. The injection of $FeCl_3$ operated to precipitate phosphates before filtration was found to accelerate the aggregation process in the early phase (< one year) of operation of the sludge.

Key words

Vertical flow constructed wetland; Treatment wetland; Sludge; deposit; Organic matter; Humification

INTRODUCTION

French Vertical Flow Constructed Wetlands (French VFCWs) have demonstrated their efficiency for the treatment of wastewaters at a low cost and with easy operation and maintenance (Sundaravadivel & Vigneswaran, 2001). In France, they have become the process selected by a majority of rural communities below 2 000 Population Equivalent for the treatment of domestic wastewaters (Bellin, 2016). The so-called "classical French system" is composed of two successive stages of filters where the first stage is fed by unsettled wastewater.

This treatment stage may be complemented with additional operations such as aerobic biological trickling filter and $FeCl_3$ injection. The percolation of unsettled wastewater through the first stage filters results in the formation of a sludge deposit layer at their surface due to the retention of suspended solids. This layer has positive roles in the treatment performance, with respect to suspended solid retention and the degradation and/or sorption of soluble pollutants (Chazarenc & Merlin, 2005; Kim et al., 2013; Molle, 2014). The growth of the surface layer's thickness with time may also reduce the permeability of the filter and lead to clogging, thereby reducing treatment performance. Removing the sludge deposits may then become necessary after 10 to 20 years of operation to restore optimal hydraulic conditions. Yet, field observations have shown that clogging may be observed at an early stage after only a few years in some plants, whereas other plants would not show any clogging problem even after 15 years of operation. Although several hypotheses may be proposed as potential explanations of the differences observed (Kim & Forquet, 2016; Knowles et al., 2011; Nivala et al., 2012), the dominant factors governing the characteristics of the surface deposits and the mechanisms of their evolution in time are not yet clearly identified. Only few studies have focused on the analysis and characterization of the sludge deposits in relation with their origins and the operational and environmental conditions of the treatment plants (Bois et al., 2015; Caselles-Osorio et al., 2007; Chazarenc & Merlin, 2005; Johannesson et al., 2015). With regards to clogging problems, particle size distribution in the sludge deposits is one of the key parameters to be considered as reported for other types of materials such as sediments or soils (Chen et al., 2016; Kukla et al., 2012).

It is also well known in soils and sediments sciences that the contents, nature and structure of organic matter plays a major role in the granular structure of the media, its stability over time and its sensitivity to environmental conditions (Badin et al., 2009; Boix-Fayos et al., 2001; Bronick & Lal, 2005; Six et al., 2004). Organic matter acts as a glue or a cement binding together soil particles, thereby allowing the soil particles to aggregate into relatively stable lumps called soil aggregates.

In this study, a panel of fourteen French VFCW full-scale treatment plants was constituted according to the design and operational conditions of the plants. Representative samples of their surface sludge deposits were analyzed for their contents in organic matter and major mineral elements, particle size distribution, and dynamic vapor sorption to compare their (micro) structure and evaluate the factors of influence The objective of the study was to contribute to the description of the sludge deposits characteristics and their dynamics of evolution which may control the development of clogging.

MATERIALS AND METHODS

Sites of investigation

Fourteen French VFCWs plants located in the east of France were selected as the full-scale sites from which sludge samples would be taken. Designed to treat mainly domestic wastewater, these units were considered representative of different types of process chains (Figure 1 and Table 1).

Table 1 Process types, treatment chain and operational parameters in the 14 selected French VFCW plants

Process type designation	VFCW plants	Sand trap	Additional treatments	Partially flooded filter	Number of years of operation at sampling date	Nominal capacity expressed in Population Equivalent
Classical French VFCW	**BAG1**	Yes	No	No	11	1100
	BAG2	No			8	500
	SABAG	No			7	800
	VIL	No			7	350
	BAG3	No			4	290
	PRE	No			1	700
	RAM	No			0.5	350
AZOE®	**BAY**	No	Trickling filter	No	7	1200
	MIN	No			6	1000
AZOE-N®	**NEU**	Yes		Yes	4	1600
AZOE-NP®	**VER**	No	Trickling filter and $FeCl_3$ injection	Yes	11	1100
	ORB	Yes			5	1100
	COR	No			0.5	1000
AZOE-P®	**MAT**	Yes		No	5	1600

The first type was based on the design of the so-called "classical French system", considered here as the reference process line. It comprised sieving operations of the inflow wastewater and a sand trap in some cases (stage number 1 in Figure 1) to remove coarse solids, followed by the surface loading of the influent (stage number 4) at the surface of a first and then a second stage of VFCW. To improve the performance of this reference process chain, the following additional treatments were designed by the French company SCIRPE. The corresponding process chains were patented under the registered trademarks AZOE®, AZOE-P®, AZOE-N® and AZOE-NP® as defined below:

- Additional treatment of inflow wastewater on aerobic biological trickling filter (TF) to increase carbon removal and nitrification (stage number 2)
- Injection of $FeCl_3$ into TF outflow for phosphates precipitation (stage number 3).
- Adjustable level of saturation of the first-stage filter (stage number 4), from fully drained (unsaturated) in the reference classical French system and in AZOE® and AZOE-P® processes to partially saturated in AZOE-N® and AZOE-NP® to allow nitrification in the upper aerated zone and denitrification in the lower non-aerated zone (patent EP1857419A1; PCT/EP2012/058119).

The process chains in operation in the different treatment plants of the study are summarized in Table 1. Stages 1 and 4 shown in Figure 1 were common to all the plants. The treatment plants differed by the implementation or not of stages 2 and 3, as detailed in Table 1. The operating conditions of the plants were described in more details in previous articles (Kim et al., 2013; Kim et al., 2014).

The selected plants differed not only by the operations in the treatment chain (Figure 1 and Table 1) but also with respect to other parameters, such as the number of years of operation, the nominal capacity, the peak flow, the total area of VFCW stages (Table 1), and other environmental factors.

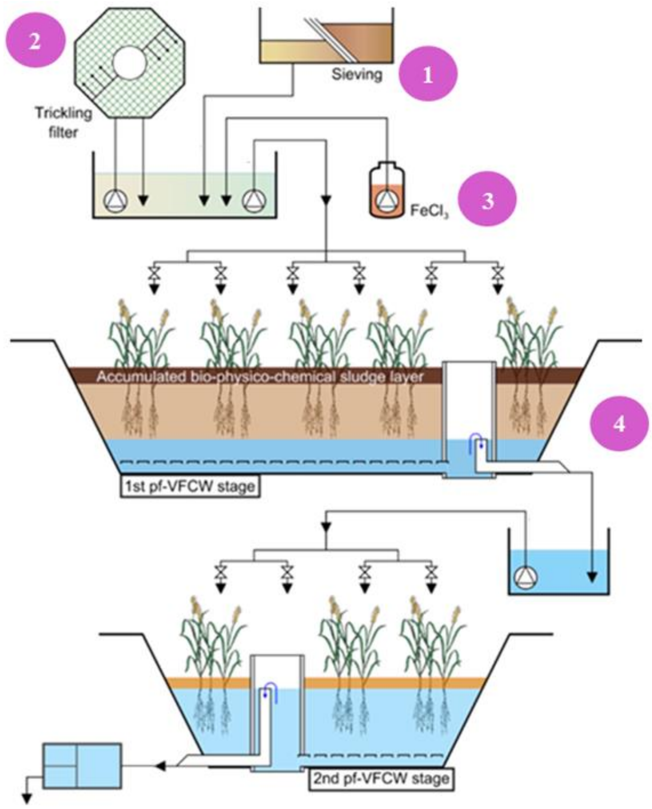

Figure 1 Simplified diagram of VFCW plants selected showing [1] the presence or not of a sand trap, the possible pretreatment with: [2] a trickling filter and [3] a $FeCl_3$ injection, and [4] the possible nitrogen treatment with a partially flooded stage of filter (from Kim et al., 2013)

Sampling and samples preparation

Surface sludge deposits were sampled between January and March 2015, except for some plants which were sampled in November 2015 (plant referenced as COR) and February 2017 (plant referenced as PRE and RAM). In each plant, the whole depth of the sludge layer was sampled from 5 to 10 spots randomly distributed. Samples from each spot were treated onsite to extract manually reeds' rhizomes and gravels, and finally mixed together to constitute the overall sample representative of the whole surface layer of the considered plant.

All samples were brought to the laboratory within a maximum of 4 hours. An aliquot of each sludge sample was directly analyzed to determine humidity and organic matter contents. Another aliquot was dried at 35°C in thin layer until constant weight, sieved to less than 1 mm to remove any residual gravels and stored at 4°C until it was analyzed for particle size distribution and other parameters.

Analytical methods

All analyses were done on three replicates of each sample. Results given in this study were the average of triplicates unless otherwise specified. Humidity of the fresh sludge samples was determined by drying at 105°C until constant mass a fresh sample of an initial mass of about 5 g (measured precisely at +/- 0.1 mg). Dry solids thereby collected were then calcined at 550°C for four hours to estimate their contents in organic matter (OM)

All other analyses were done using dried samples obtained after 1-day drying at 35°C followed by sieving to below 1 mm as indicated above. Elemental analyses were done by alkaline fusion ($LiBO_2$) followed by acid digestion and subsequent analyses of the solutions by inductively coupled plasma atomic emission spectrometry (ICP-AES). The following elements were analyzed : silicon (Si), aluminum (Al), iron (Fe), manganese (Mn), magnesium (Mg), calcium (Ca), sodium (Na), potassium (K), titanium (Ti) and phosphorus (P).

The contents in humic-like and fulvic-like substances (referred to as HULIS and FULIS, respectively) were analyzed to evaluate the humification rate of the organic matter in the sludge samples. HULIS and FULIS were extracted by suspending for 2 h under constant agitation 1g of dried sludge samples in 50mL of 0.1M sodium hydroxide aqueous solution. The suspensions were then centrifuged at 10 000 g (8000 rpm) for 15 min and vacuum filtered at 0.45µm using Sartorius cellulose acetate filters. The solutions, containing HULIS and FULIS fractions, were analyzed for total organic carbon (TOC) using a Shimadzu TOC-L analyzer, then acidified to pH 1.5 with 1M sulfuric acid aqueous solution and left at rest overnight at +4°C to allow precipitation of HULIS fraction. FULIS fraction was collected in solution by centrifugation at 6 000 g for 15min followed by filtration at 0.45µm. The solution was analyzed for TOC using the same protocol as for the HULIS + FULIS extracts. The humification rate was finally calculated as $100 \times \frac{C_{HULIS+FULIS}}{TOC}$ where $C_{HULIS+FULIS}$ was the organic carbon content measured in the HULIS + FULIS extract and TOC was the overall organic carbon content of the considered sludge sample.

Particle size distribution was analyzed using a 1190 CILAS laser particle size analyzer in a range between 0.03 and 2500 µm. The laser diffractometer used light diffraction to estimate the solid volume represented by each size of particles considered spherical. In a first series of measurements, the samples were analyzed in the form of gently stirred suspensions prepared in the outflow effluent of the respective plants of origin, previously filtered at 0.45µm, to avoid multiple scattering (Jin et al., 2004). In a second series of measurements, ultrasounds (US) were applied to the suspensions for 1 min at a power of 50 W prior to particle size analyses, in the objective to disperse possible aggregates as reported by Badin et al. (2009) and Snidaro et al. (1997) on urban sediments or activated sludge respectively. All measurements were triplicated.

The level of aggregation of the sludge particles in the different samples was indirectly assessed by quantifying the effect of ultrasounds as illustrated in Figure 2. The aggregation rate was calculated as the ratio between the fraction of the initial curve showing a decrease in the apparent size of the particles due to the application of ultrasounds (hatched surface in Figure 2) and the overall surface obtained without ultrasounds (greyed surface in Figure 2). The aggregation rate defined in this study was used to express the extent of aggregation in the sludge samples by measuring the proportion of particles which apparent size was reduced by ultrasounds.

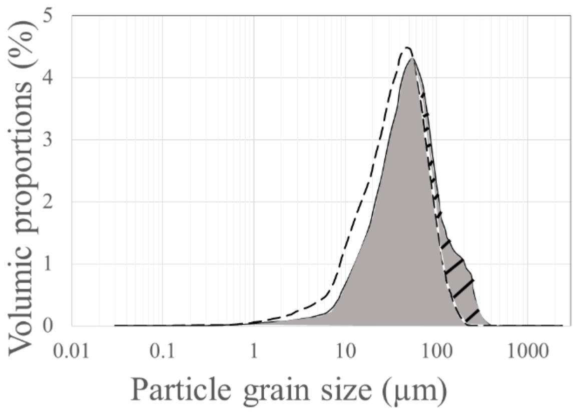

Figure 2 Illustration of the method to calculate aggregation rate from particle size distribution curves with and without ultrasounds application, with aggregation rate = $\frac{\text{Hatched surface}}{\text{Greyed surface}}$ (adapted from Badin et al., 2009).

Steam sorption analyses of dried sludge samples were performed using a DVS (Dynamic Vapor Sorption)-Advantage Elevated Temperature system. An aliquot of 20mg of each sample was placed on the sample holder, connected with a wire to a high precision balance of 0.1 µg mass resolution. The system was placed in a thermo-regulated chamber purged at a constant flow with nitrogen gas spiked with steam at controlled partial pressures P_w. The temperature during the entire experiment was kept constant at 25°C. Steam sorption/desorption isotherms were obtained by increasing the level of saturation of the flow gas (defined as the ratio of actual P_W over the saturated vapor pressure P_{sat} of water at the considered temperature) from 0 to 0.90 by increments of 0.01 and then taking it back to 0 in the same manner. Each increment in Pw was operated automatically when the rate of mass change (dm / dt) of the sample was less than 0.001% per minute. The mass of sample was acquired every 20 seconds. This technique allowed to monitor at a constant temperature the changes in moisture content within the sample as a function of the thermodynamic activity of water in the atmosphere surrounding the sample. Water activity was defined by $a_W=\frac{P_v}{P_{sat}}$, where P_v was the actual partial pressure of water and P_{sat} the saturated vapor pressure of water at the considered temperature. Since the recorded isotherms reflected the interactions between gaseous water and the solid surfaces of the samples, they provided useful information on the micro and mesometric structure of the samples.

RESULTS AND DISCUSSION

Elemental analysis

Average results from the analyses of the 14 sludge samples are given in Table 2. Organic matter (OM) contents were found to range between 50.3 and 86.2% of total dry matter (% w/ w DM). The major mineral elements were, by order of decreasing abundance, Si, Ca, Al and Fe. The contents in Si varied between ca. 2.1 and 13.3% w/w DM, Ca between 1.6 and 4.7 %, Al between 0.4 and 3.2%, and Fe between 0.2 and 5.9%. Si content in the sludge deposits from the plants with no sand trap (PRE, RAM, BAY, MIN, VER and COR) revealed surprisingly low Si contents (2.1 – 5.7% w/w). This observation was attributed in part to the fact that the gridding

/ sieving stage, present in all plants, probably acted as a sand trap when residence time was long enough. Fe concentrations in the sludge samples from the plants using $FeCl_3$ injections were logically higher than in the sludge deposits from the other plants (3.5; 3.5; 5.2 and 5.9 % w/w in VER, ORB, COR and MAT samples, respectively, vs. 0.2 to 1.4% in the other samples).

Mg, Na, K and Mn were present at lower concentrations in the sludge deposits. The analyzed concentrations were in the same order of magnitude in the different sludge samples (0.1-0.4%; 0.1-0.4%; 0.2-1.2% and 0.02-0.04% w/w DM, respectively), although MAT sample exhibited systematically the highest concentrations in these elements, as also in the major mineral elements. This observation was explained by the low OM contents of this sludge deposit (50.6 % w/w of DM), yielding to higher concentrations of the mineral fractions within the dry matter.

By comparison, activated sludge usually contain more organic matter than most French VFCW sludge deposits analyzed here, with about 70% w/w of dry matter (Alvarenga et al., 2015; Vincent, 2011). Aluminum, sodium and potassium contents in activated sludge were very close to the concentrations analyzed here in VFCW sludge deposits (11.7%, 2.6%, 0.3% and 0.3% w/w of dry matter respectively) (Magdziarz & Wilk, 2013). Conversely, they reported iron, magnesium and calcium contents in activated sludge (4.8%, 8.5% and 16.8% w/w of dry matter respectively) higher than observed here on VFCW samples. On the other hand, Technosol materials from infiltration urban basins were reported to be much lower in OM content (<20% w / w of dry matter) as compared to sludge deposits from VFCWs, whereas their concentrations in major mineral elements (Si, Al, Fe, Mg, Ca), although variable, were higher and Mn, Na and K contents very close (Badin et al., 2009).

Table 2 Composition of sludge deposits from the selected VFCW plants.
Results are given as g of OM or each element in 100g of DM

Ref	OM(1)	Si(2)	Ca(2)	Al(3)	Fe(2)	Mg(3)	Na(4)	K(2)	Mn(3)	Ti(3)
BAG1	59.0	7.7	2.6	2.1	1.0	0.3	0.2	0.5	0.02	0.2
BAG2	57.4	13.3	2.9	2.0	0.9	0.3	0.2	0.7	0.01	0.2
SABAG	60.3	11.6	2.6	1.8	1.4	0.3	0.2	0.6	0.04	0.2
VIL	60.9	10.5	2.4	2.4	1.2	0.3	0.1	0.5	0.01	0.3
BAG3	50.3	13.2	3.5	2.4	1.4	0.3	0.3	0.7	0.02	0.2
PRE	86.2	2.1	2.5	0.4	0.2	0.1	0.1	0.2	<D.L.	0.1
RAM	84.3	3.4	3.2	0.6	0.3	0.2	0.1	0.2	<D.L.	0.1
BAY	70.5	3.3	4.7	1.5	0.5	0.3	0.1	0.3	0.01	0.2
MIN	73.5	5.0	3.5	1.3	0.6	0.4	0.2	0.4	0.02	0.3
NEU	58.6	9.6	3.7	2.3	1.2	0.4	0.3	0.7	0.04	0.2
VER	62.0	5.7	3.8	2.1	3.5	0.3	0.1	0.4	0.02	0.2
ORB	58.2	7.3	3.8	2.0	3.5	0.3	0.1	0.5	0.03	0.2
COR	72.0	2.8	4.6	0.8	5.2	0.3	0.2	0.5	0.02	0.2
MAT	50.6	11.2	1.6	3.2	5.9	0.4	0.4	1.2	0.5	0.3

OM: Organic Matter; DM: Dry Matter; DL = Detection Limit

(1) Analytical results on the replicates of all samples did not exceed a range of ±2.5%

(2) Relative uncertainty = 5%; (3) Relative uncertainty = 10%; (4) Relative uncertainty = 15%

Particle size distribution

Particle size distribution curves are shown in Figure 3. Table 3 reports the values of the key parameters derived from each graph, namely the upper size limit of the 10% smallest particles d_{10}, the lower size limit of the 10% biggest particles d_{90}, and the particle size at the peak of the distribution curves d_{max}. It can be seen that the distribution curves obtained with non-sonicated aqueous suspensions were very similar for all the samples. Table 3 showed that without sonication the size of more than 80% of the particles was found in the different samples to range between a d_{10} of 9.4 to 16.0 µm and a d_{90} of 115.1 to 207.0 µm, with a d_{max} between 32 and 63 µm. The particle size in each sample was therefore quite narrowly distributed as confirmed by the low d_{90}/d_{10} ratios ranging from 8.1 to 17.4 (Vincent, 2011). These characteristics suggested that French VFCW surface sludge deposits exhibited common characteristics that may allow to group them within a special typology of sludge materials. Published studies on similar materials reported different characteristics for activated sludge with a d_{max} around 100 - 125 µm and a d_{90}/d_{10} ratio around 8 (Snidaro et al., 1997; Vincent, 2011), or for Technosol materials with a d_{max} between 400 and 600 µm with a possible bimodal distribution (Badin et al., 2009).

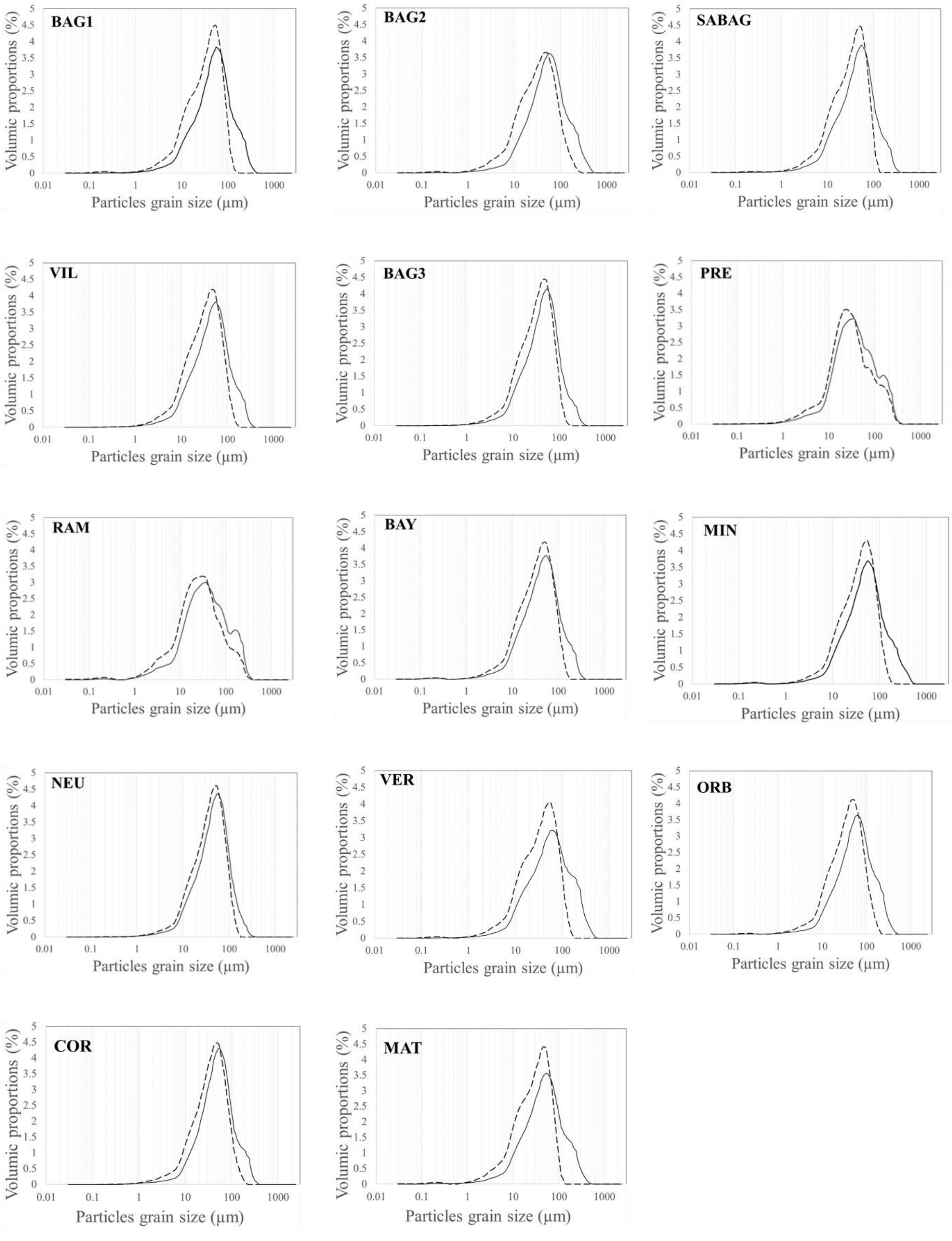

Figure 3 Frequency curves of particle size distribution obtained by laser diffractometry of sludge samples in suspension in the outflow effluent previously filtered at 0.45 µm
(Solid line: non-sonicated suspensions; dotted lines: suspensions sonicated for 1 min at 50 W)

Table 3 Key parameters of particle size distribution in the surface sludge deposits

VFCW plants	Without ultrasounds (US)				With US	
	d_{max}	d_{10}	d_{90}	d_{90}/d_{10}	d_{max}	Aggregation rate %
BAG1	56	13.4	161.2	12.1	53	23.3
BAG2	56	14.9	189.8	12.8	45	21.1
SABAG	56	12.2	135.2	11.1	53	20.5
VIL	56	12.8	142.4	11.1	50	19.2
BAG3	56	12.9	121.7	9.5	50	17.2
PRE	32	11.0	153.7	14.0	25	10.4
RAM	36	9.4	163.2	17.4	32	13.7
BAY	53	12.9	139.3	10.8	50	14.8
MIN	56	14.1	185.5	13.2	53	18.1
NEU	56	14.2	115.1	8.1	53	12.3
VER	63	13.6	207.0	15.3	56	24.7
ORB	63	16.0	189.6	11.9	50	22.1
COR	53	16.0	142.0	8.9	50	16.8
MAT	53	12.7	173.9	13.7	50	27.0

Results shown in Figure 3 and Table 3 were further analyzed to assess possible differences in particle size distribution of the samples that could be attributed to the process parameters differentiating their plants of origin. It was observed that samples taken from the most recent plants (RAM and PRE) exhibited significant differences with the others. Hence, the particle size corresponding to the peak of their respective distribution curve (d_{max} in Table 3) was 32 and 36 µm in PRE and RAM samples from the youngest plants whereas it ranged between 53 and 63 µm in the other samples. The volumetric proportion of particles at d_{max} was lower in PRE and RAM samples than in most other samples (around 3.0 and 4.5%, respectively). Furthermore, the size corresponding to d_{10} limit was 11.0 µm in PRE sludge and 9.4 µm in RAM sludge while it ranged from 12.2 to 16.0 µm in the other samples. The particle size distribution recorded for the sludge deposits from young plants PRE and RAM were actually close to those measured on suspended solids in inflow domestic wastewater (d_{max}, d_{10} and d_{90} values around 20 µm, 10 µm and 166 µm, respectively) (Marquet et al., 1999). However, sludge deposits from COR plant, which was also a young plant of less than 1 year of operation (Table 1), exhibited particle size characteristics close to the deposits from older rather than younger plants (Table 3). One probable explanation was that PRE and RAM plants were operated without any pretreatments (Table 1), whereas the process line in COR plant included pretreatments on a biological trickling filter followed by $FeCl_3$ injection. The flocculating effects of $FeCl_3$ probably induced the formation of particles of larger sizes from the very beginning of operation of the plant (El Samrani, 2003). Similarly, the presence in COR of a biological trickling filter as a pretreatment of the inflow may also have contributed to increasing the overall particle size of the sludge deposits by the detachment of biofilm fragments (Marquet et al., 1999). Yet, the pretreatment effects on the particle size, although visible on the sludge deposits from the young plants RAM, PRE and COR, appeared less significant on the deposits from the oldest ones (Table 3). It was therefore concluded that the process of *in situ* ageing of the sludge deposits induced their evolution towards a similar global state after a few years of operation, regardless of the initial characteristics of the deposits.

In order to investigate the possible mechanisms of ageing on particle size distribution of the surface deposits and the possible effects of different factors on these phenomena, the level of aggregation of the particles was investigated.

Nature and level of aggregation of the sludge particles in the VFCW surface deposits

To evaluate the aggregation phenomenon in the sludge deposits, the apparent particle size distribution obtained for each sample with and without the application of ultrasounds was compared (Figure 2). Many authors clearly showed that the application of ultrasounds to soil suspensions allowed to break the interactions between the soil particles, resulting in the dispersion of soil aggregates (Badin et al., 2009; Kaiser & Asefaw Berhe, 2014).

The particle size distribution curves observed without ultrasounds were unimodal as discussed above, with a d_{max} peak around 52 (±7) µm, a slight shoulder observed at higher particle sizes around 250 µm, and another shoulder around 71µm for PRE and RAM samples (Figure 2). It was observed that for most of the samples, the application of ultrasounds led to size distribution curves where the shoulder around 250 µm was not visible anymore (except in PRE and RAM samples where the effect was not as strong), whereas a new shoulder was observed around 10 µm. Furthermore, the d_{max} peak was slightly shifted from 32-63 µm without sonication to 25-56 µm after sonication. These observations indicated that the sludge particles were present in all samples in the form of aggregates which were partly dispersed by ultrasounds. The calculated aggregation rates varied from 10.4 to 27.0% as shown in Table 3.

Figure 4 illustrated the influence of organic matter contents of the sludge deposits (a) and the operating time of the plants (b). It revealed that sludge deposits from young plants, such as PRE, RAM and COR, where OM contents were high, were those exhibiting the smallest aggregation rates. Conversely, sludge deposits from older plants appeared to tend towards a higher aggregation rate close to 20-25%. The additional treatment steps (namely aerobic biological trickling filter and $FeCl_3$ injection) operated in the plants shown in red in Figure 4 (COR, MAT, ORB and VER samples) were found to increase the level of aggregation in their surface sludge deposits as compared to the sludge deposits from the treatment plants shown in blue where no additional treatments were operated. The effect of the trickling filter alone in the plants shown in green (NEU, MIN and BAY samples) was found however insignificant, indicating therefore that the injection of $FeCl_3$ was the operational variable with the highest influence.

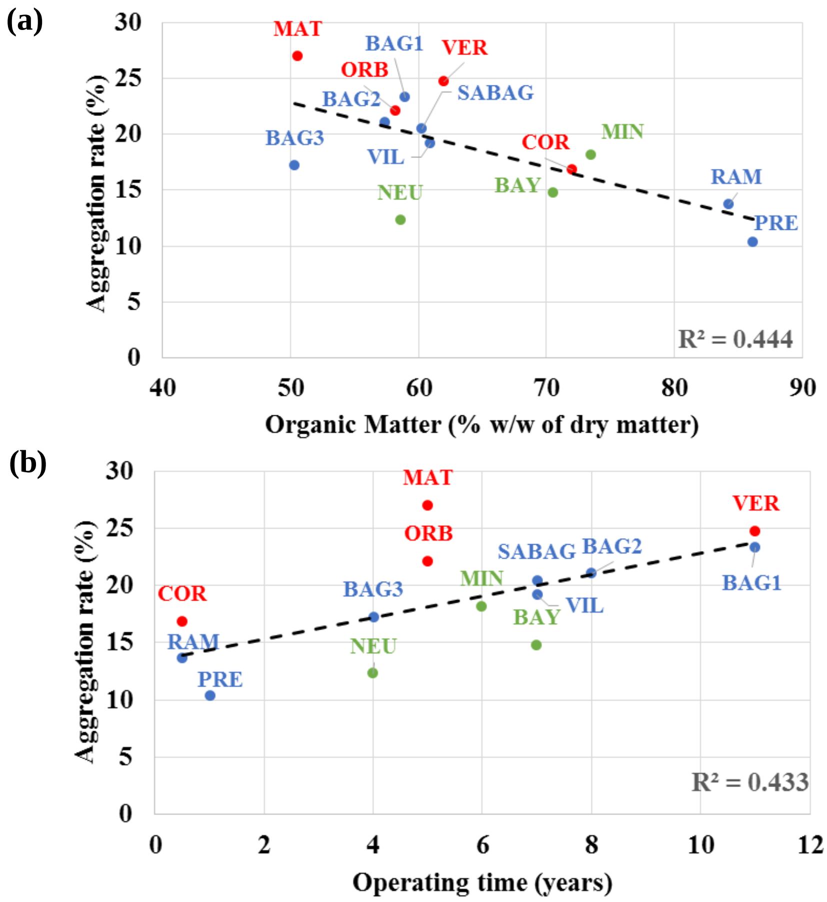

Figure 4 Correlation between the level of aggregation of the 14 sludge samples and (a) OM contents and (b) the number of years of operation of the plants of origin

Interactions between particulate and soluble organic matter (POM and SOM), fine mineral particles (clay), and mineral polyvalent cations have been reported to control the development of soils' structure (Bronick & Lal, 2005; Six et al., 2004). Our results however showed that the sludge samples with the highest OM contents revealed the lowest aggregation rates. Although apparently in contradiction with the mechanisms of aggregation generally admitted, this observation may be attributed to the nature and form of the fresh organic matter in the samples studied here. Since domestic wastewaters were by far the predominant type of inflow wastewater received in the different French VFCW plants, the organic matter at the origin of the sludge deposits was most likely present in the form of amorphous deformable macrostructure, such as mucilages (Oades, 1984). It was also described as a polymer-mesh phase made of three-dimensional entanglement of macromolecules (Cuypers et al., 2002; Pignaletto, 1998). In older plants, sludge deposits accumulated at the surface of the filters were progressively aged over the years of operation of the plant, under the effects of various factors. In particular, hydrolysis and mineralization of the most readily biodegradable organic fractions, humification of the more recalcitrant fractions, combined with the effects of wet / dry alternations arising from the intermittent feeding and resting conditions (Denef et al., 2001) were likely to induce drastic modifications in the structure of organic matter within sludge deposits. The residual organic matter could then develop stronger interactions with polyvalent mineral ions and mineral particles, and induce the formation of microaggregates within the initial organic macrostructure of the fresh organic matter as already described in soil systems by Oades (1984). These hypotheses and the influence of other possible factors were further investigated by a statistical treatment of the experimental dataset gathered in the study.

Statistical analyses of dataset

The possible correlations between the variables used to characterize the samples were investigated by a Principal Components Analysis (PCA). Figure 5 shows the position of the selected variables on the correlation circle (a) and a plot of individual data points (b) on the plane represented by the first 2 components. They accounted for close to 80% of the overall variance (59.2% and 14.2%, respectively), indicating that the representation in PC1xPC2 plane carried most of the statistical information. All the variables used to characterize the samples were positioned very closely to the correlation circle, meaning that their influences were very well represented in the analysis.

It can be seen that the first component, accounting for 59.2% of the total variance, was strongly defined by the organic and mineral contents of the samples. The variables of strongest influence were: (i) the contents in the major mineral elements Si, Al and Na+K, (ii) the OM content which was anti-correlated to Na+K contents, and (iii) the aggregation rate which was anti-correlated to OM contents and positively correlated with Si, Al, and Na+K contents. The second component PC2, accounting for 14.2% of the total variance, was not well defined by any of the variables, although Fe concentration and the number of years of the plants showed a certain contribution. The anti-correlation between organic content and Si - Al contents on PC1 was rather logical since these variables were intrinsically complementary to each other. Within the dry matter of the samples, a high (resp. low) proportion of organic matter (OM) implies a low (resp. high) contents in mineral fraction in which Al and Si were the major two elements. The anti-correlation between aggregation rate and OM confirmed the observations discussed in the previous section (Figure 4). Sludge samples with the highest OM contents were those from the most recent French VFCW plants PRE, RAM and COR. Figure 5 clearly showed that the sludge deposits from plants PRE and RAM were positioned very close to OM content variable. COR sample, also taken from a young plant (Table 1), was also positioned to the right hand side of the diagram strongly influenced by OM variable, but was in a lower position than PRE and RAM. This was attributed to the injection of $FeCl_3$ in COR. The other samples exhibited a much lower OM contents and furthermore their organic matter was aged *in situ* for several years thereby potentially allowing a stronger effect on aggregation as compared to the organic matter in the young plants PRE, RAM and COR. To confirm these hypothesis, the humification rate (expressed in % of TOC) was used in addition to the OM contents in order to evaluate whether these complex organic structures formed over time during the *in situ* ageing of the sludge deposits played a role in the formation and stabilization of aggregates as reported in soil systems (Bronick & Lal, 2005). Figure 5 showed that the humification rate was indeed strongly correlated to the aggregation rate.

This observation indicated that the evolution of organic matter in time contributed to the formation of aggregates in the oldest sludge samples. On the contrary, the major part of organic matter within the youngest sludge deposits was not in a suitable form to promote aggregation.

However, the particle size distribution curves of sludge deposits from young plants (RAM and PRE) showed the same shoulder (or even more visible) around 250 µm as the older samples (Figure 1). Since this shoulder remained visible after ultrasounds application to the youngest samples, it was concluded that fresh organic matter included the presence of macrostructures around 250 µm which were however poorly dispersed by ultrasounds. This could be explained by the deformable structure of fresh organic matter from domestic wastewater.

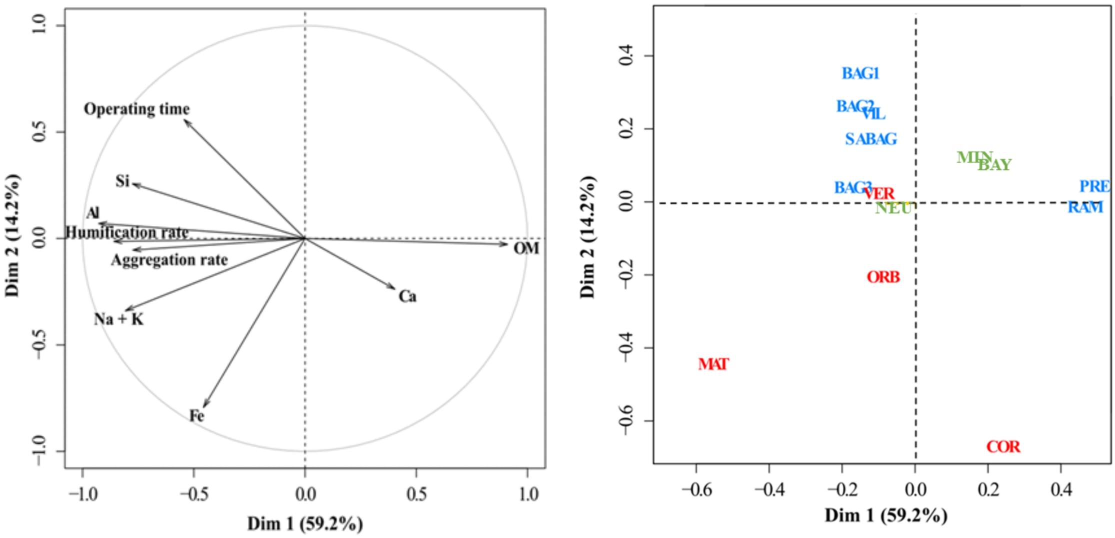

Figure 5 Plot of variables on the correlation circle (a) and PCA plot of individual data (b), illustrating the possible factors of influence of aggregation in sludge deposits

The mechanisms of aggregation have been extensively investigated in soil sciences. Although different in nature and conditions of evolution, some analogies can be made between soil systems and French VFCW surface sludge deposits in an attempt to explain the observed results. Several theories have been developed (Six et al., 2004). Edwards and Bremner (1967), described the formation of microaggregates (< 250 mm) as a solid-phase reaction between clay particles, and / or polyvalent cations (Ca, Fe, Al) and / or organic matter. The description was further modified and deepened by the “aggregate hierarchy concept” proposed by Tisdall and Oades (1982), which considered several stages where free particles would bind together to form stable microaggregates (20-250 mm) which could bind together into less stable macroaggregates. The two stages were firstly considered to occur successively, but the theory was further modified by considering that macroaggregates could be formed first via the coating of particulate organic matter POM (such as organic fragments from roots decay, etc.) within bio-produced mucilages, which would then bind to microaggregates by soluble organic matter (SOM) interactions. This model was subsequently validated on several soils (Beare et al., 1994; Elliott & Coleman, 1988). Based on our results, it appears also suitable to describe the aggregation phenomena involved in the system studied here, although the organic matter is of different nature and the conditions of evolution quite different. The clear correlation observed in Figure 5 between the aggregation rate and the humification rate tends to confirm the validity of the aggregation model.

Investigation of porous structure using Dynamic Vapor Sorption (DVS)

The alternation of feed and rest periods in the operation of the French VFCW plants may cause strong variations in water content within the surface sludge layer. These variations are likely to affect the physical state of water within the sludge deposits, with consequences on the particles aggregation and the cohesion of the aggregates (Bronick & Lal, 2005; Six et al., 2004). Further studies were therefore conducted to characterize the physical state of water within a selection of samples made of the sludge deposits from two of the youngest plants (COR and RAM, respectively with and without $FeCl_3$ injection) and two sludge deposits from older plants (VER and MAT).

Dynamic Vapor Sorption (DVS) was measured on these four samples as a function of water activity a_w. Sigmoïdal isotherms were obtained at $a_w < 1$ as shown in Figure 6, corresponding to type II in Brunauer's classification (García-Bernet et al., 2011; Vaxelaire & Cezac, 2004). Each isotherm can be divided into three regions corresponding to different states of bound water, namely (i) hydration water at $a_w < 0.1$ where water is very strongly bound to the accessible surfaces of the solid particles in the form of a mono molecular layer; (ii) vicinal water at a_w comprised between 0.1 and 0.7 where additional layers of molecules of water are less strongly bound; and (iii) capillary water at $a_w > 0.7$ where a continuous film of water raise in the porous medium by connecting the micropores. Free water, which is mobile under the effect of gravity forces, can be estimated by extrapolation of the isotherms at $a_w = 1$; but this determination is generally not accurate and has not been done here. Sorption isotherms (Figure 6) were used to calculate the relative amounts of water under the 3 different states and the results are shown in Table 4. The isotherms also allowed to calculate various parameters characteristic of the samples' porous structure, since the sorption of water under the three considered physical states was related to the presence of available micro and mesopores.

It can be seen on Figure 6 that under water activities below 0.1 (mono molecular layer of sorption), the adsorption isotherms of VER and MAT were superposed. The calculated water contents were 6.12% and 5.51% DM and mono molecular water layers surface areas were 141 $m^2.g^{-1}$ of DM and 113 $m^2.g^{-1}$ of DM, respectively (Table 4). At water activities between 0.1 and 0.7, corresponding to vicinal water, the isotherms of VER and MAT samples were clearly distinct one from the other, whereas COR and RAM isotherms were very close to each other. The isotherms revealed that the amounts of vicinal water, and the corresponding specific surface of micropores, were increasing with the age of the sludge deposits analyzed. Vicinal water content was around 8% in COR and RAM samples (less than 1 y of age), 10.4% in MAT (5 y) and 11.3% in VER (11 y), and micropores specific surface areas were 136 $m^2.g^{-1}$ of DM in RAM, 195 $m^2.g^{-1}$ of DM in COR, 195 $m^2.g^{-1}$ of DM in MAT and 218 $m^2.g^{-1}$ of DM in VER. The same observation can be done with capillary water and the corresponding mesopores surface area.

These observations revealed that the fine porous structure of the sludge deposits was increased in the ageing process over the years of operation of their French VFCW plants of origin, thereby improving water retention capacity of the sludge layer. This finding also confirmed the increased aggregation rate observed with time in Figure 2.

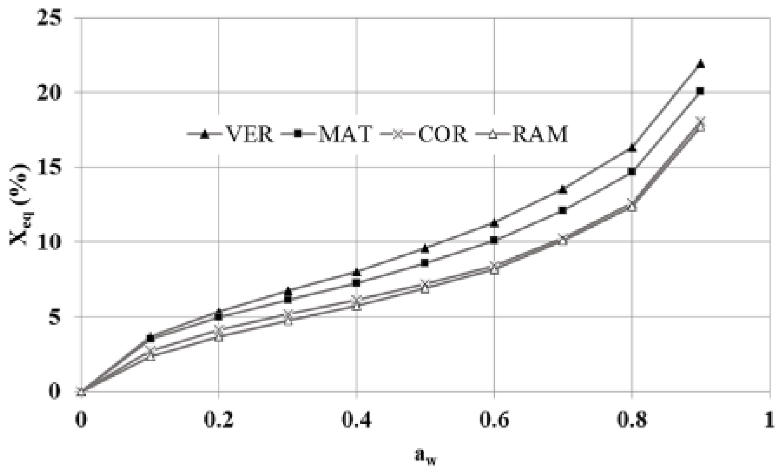

Figure 6 Water sorption isotherms of sludge deposits from young (< 1 y, COR and RAM) or older French VFCW plants (VER and MAT, resp. 11 and 5 years)

Table 4 Contents in different types of water (% of dry matter) and specific surface areas calculated from sorption isotherms (in $m^2.g^{-1}$ of dry matter)

a_w	State of water	VER	MAT	COR	RAM
< 0.1	Monolayer water	6.12	5.51	4.63	3.54
0.1 – 0.7	Multilayer water	11.3	10.4	8.10	8.00
> 0.7	Capillary water	8.20	8.50	11.2	11.0
	Sum = Bound water	*25.5*	*24.4*	*23.9*	*22.5*
< 0.1	Monolayer water surface area	141	113	105	88
0.1 – 0.7	Micropore (< 2nm) surface area	218	195	190	136
> 0.7	Mesopore (2-50 nm) surface area	17.8	15.5	14.0	13.5

CONCLUSION

Results showed that surface sludge deposits from French VFCWs have common characteristics, notably in terms of their particle size distribution, which make them a special typology of sludge materials as compared to activated sludge for example. Results from the analysis of sludge deposits also provided strong evidences on the possible mechanisms of evolution of French VFCW sludge deposits over the years of operation of the plants. Experimental data suggested that ageing of fresh sludge deposits induced the formation and integration of stable microaggregates within the initial macrostructure of the fresh organic matter, as proposed in soil systems by Oades (1984) although the origin of organic matter was here different than in soils. This model allowed to explain the increase of micro and mesoporosities of the sludge deposits (observed by DVS) by the formation of stable microaggregates within the deformable polymer-mesh fresh organic matter. This mechanism of aggregation, along with the progressive humification of organic matter shown by the increase of HULIS and FULIS contents, also allowed to explain the increase in bound water contents observed by DVS.

$FeCl_3$ injections used in some plants to precipitate phosphorus was found to accelerate the aggregation of sludge particles in the young age of their evolution but the final state of pseudo equilibrium reached after several years was apparently similar. The humification rate in the sludge deposits was identified by PCA statistical treatment of the experimental dataset as the key variable governing the aggregation process.

The pore structure of the surface sludge layer is known to play an important role in the infiltration of wastewater during the operation of the plants. The mechanisms of evolutions described in this study may therefore allow to better control clogging and its negative operational consequences (Kim & Forquet, 2016; Molle, 2014). The micro and meso structure of the sludge deposits may also affect the penetration of air within the sludge layer. The evolutions observed here may therefore also have direct incidences on the overall performance of the VFCW systems.

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