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Dewaterability of MBR sludge loaded with tannery wastewater

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ABSTRACT

Dewaterability of chromium rich sludge, typical of tanning wastewater treatment plant, was tested in the following research. Sludge was collected from an aerobic reactor of membrane bioreactor (MBR) pilot plant, treating a synthetic influent containing a concentration of 10 mg l^{-1} of total chromium. Specific resistance to filtration (SRF) and time to filter (TTF) were evaluated to characterise MBR chromium rich sludge (MBRcrs) dewaterability. Four different sets of experiments and more than 270 tests were performed and evaluated. SRF for MBRcrs in normal condition was $2.58 \cdot 10^{11}$ m kg^{-1}; sludge thickening produced better dewaterability condition but not really considerable, SRF value decrease was only 8%; conditioning experiment, in most of the concentrations and combinations tested, did not improve considerably MBRcrs dewaterability. The results open the way to develop a simplified MBRcrs treatment plant as an effective and efficient solution to reduce sludge treatment and disposal costs. It was shown thickening is not so useful as for conventional activated sludge (CAS) plant; a stabilisation step is not needed because MBR plants do not have a first clarifier and biological sludge is stable; dewatering phase does not require mandatory conditioning before dewatering processes because SRF value is $<10^{12}$ m kg^{-1}.

Keywords: MBR; Flat sheet membrane; Dewaterability; Chromium; Tannery; SRF; TTF

1. Introduction

Membrane use in industry is consolidated as filtration technique for processes and for wastewater treatment [1–3]. In the case of membrane coupled with bioreactor, the same success can be claimed for municipal wastewater treatment, where a better knowledge of this technology and operating costs decrease will lead to an increase in the number of MBR plants in the next years [1,4].

The development of membrane technology opened the way to new wastewater treatment as in the case of tannery industries; in fact, intrinsic difficulties related to tanning wastewater treatment, because of its very diverse composition and considerable environmental damage, due to outflow discharge, are well known. Many researches were performed to evaluate the use of membrane for wastewater filtration both on real tanning wastewater and on aqueous solutions containing only chromium sulphate ($Cr_2(SO_4)_3$), used in tannery industries. The results showed high heavy metal efficiency removal for a wide range of membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [5–8].

At present, tanning wastewaters at full scale are usually pre-treated with physical-chemical processes, followed by conventional biological processes; these solutions are particularly expensive, both for considerable quantity of reagents required and for high amount of sludge produced.

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The idea of treating chrome tanning wastewaters with MBR is rather recent and until now very few researches have been conducted in this regard [9,10]. The results are positive, but still there is uncertainty as to which substance is inhibitor of biological processes and yet no one has analyzed sludge dewaterability to see if such treatment is actually beneficial to reducing sludge disposal costs.

In fact, to dispose wastewater treatment plants by-products is one of the main problems in plants management; almost 50% of the budget [11]. Furthermore sludge from tannery industries is a hazardous waste due to chromium content, so sludge agriculture use cannot be pursued but it has to be disposed in waste special landfill. So, the treatment and the disposal of wastewater treatment plants sludge are big issues; evaluating sludge dewaterability characteristics is mandatory to find out the best technologies to reduce its treatment and disposal costs. Usually, design and management parameters of sludge treatment plant are obtained through laboratory tests or tests on pilot plants, since variability of sludge characteristics makes performances forecast of dewaterability systems difficult.

The same issue is true for MBR sludge; because MBR plants will be increasing considerably in the next years [1,4], but few data and researches finalized to evaluate MBR sludge dewaterability characteristics are available at the moment [12–14]. Furthermore microbiological differences exist between CAS and MBR sludge [15,16], which could produce a better dewaterable MBR sludge than CAS. Finally, MBR treatment plants, usually, do not have first clarifiers, but more effective pre-treatments such as screening. So sludge to be treated comes only from biological reactor and usually has a Sludge Retention Time (SRT) that does not require stabilization.

Hence, in this study, MBR chromium rich sludge dewaterability characteristics were evaluated; the results open the way to simplified MBR sludge treatment plants as an effective solution to reduce sludge treatment and disposal costs, and promote MBR systems to treat tannery wastewaters.

2. Materials and methods

2.1. MBR set-up

MBRcrs was collected from an aerobic reactor of MBR pilot plant. It has treated a synthetic influent with a composition similar to domestic wastewater since December 2007, plus a concentration of 10 mg l^{-1} of total chromium as chromium sulphate ($Cr_2(SO_4)_3$), since May 2008.

The pilot-scale MBR was designed to achieve effluent quality good for reuse (EU Water Framework Directive 91/271/EEC) according to the Italian law D.M. 185/2003. Two reactors, anoxic and aerobic, in series, following a pre-denitrification type configuration, were configured based on simulations using Esposito's model [17] with default model parameters at 20 °C. The information used were: a membrane surface area (0.11 m^2), Total Suspended Solids (TSS) concentration (8–20 g l^{-1}) and filtration flux (5–25 l m^{-2} h^{-1}). TSS concentration was set in the common range used in full-scale MBR. Filtration flux also was referred to filtration flux range in full-scale Flat Sheet (FS) MBR. An influent synthetic wastewater similar to domestic wastewater was used. The influent flow rate was determined by the size of the membrane module and filtration flux (19.8 l m^{-2} h^{-1}). Amount of waste sludge was decreased in order to increase TSS concentration and SRT so as to have environmental condition changes more resistant sludge [18]. Recirculation flow rate (Qr) from aerobic compartment to anoxic one was increased to achieve higher nitrate removal; aerobic reactor volume was also increased, due to technical reasons connected to the membrane. In conclusion, MBR consists of an anoxic compartment and an aerobic compartment that is provided with two Kubota flat sheet membranes characterised by a surface area of 0.11 m^2 each and a nominal pore size of 0.4 μm; the main parameters which characterised the pilot plant are summarised in Table 1.

2.2. Analytical measurement

Specific resistance to filtration (SRF) and time to filter (TTF) were evaluated to characterise dewaterability of MBR chromium rich sludge. SRF is a parameter that indicates sludge attitude to being dewatered by filtration and its values were calculated according to Eq. (1) and are measured in m kg^{-1}.

$$SRF = \frac{2mA^2\Delta p}{\mu p_{\mathrm{p}}} \tag{1}$$

where A = filter surface; Δp = pressure difference between the two filter faces; μ = permeate viscosity

Table 1
Pilot plant characteristics

Parameter	Value	Unit
Influent flow rate	105	ld^{-1}
Qr	315	ld^{-1}
Sludge waste flow rate	0.8	ld^{-1}
Anoxic reactor volume	13.6	l
Aerobic reactor volume	30.8	l
SRT	55.5	d
TSS	9.8	gl^{-1}
VSS (Volatile Suspended Solids)	7.43	gl^{-1}
HRT (Hydraulic Retention Time)	10.2	h

(to assume equal to the water one at the same temperature); m = angular coefficient of the straight line interpolating experimental values in the 2D plot (V; t/V);

$$p_P = \frac{P_s}{V_f} \quad (2)$$

represents the dry sludge mass for unit of filtered volume;

$$P_s = C_0 V_{sludge} - C_f V_f \quad (3)$$

represents sludge panel mass stoked on the filter. C_0 and C_f are the TSS in the sludge and in the permeate respectively, and V_{sludge} and V_f are the relative volumes. The tests showed that suspended solids present in the permeate can be neglected and, therefore, the $C_f V_f$ term too.

The tests were performed according to the standard methods [19], so they were stopped when one of the following conditions occurred:

- breaching of the sludge panel stoked on the filter and decrease of Δp as consequence;
- experimental values deviation from the straight line in the 2D plot (V; t/V);
- overcoming of the 60 min as filtration time.

TTF is defined as the necessary time to ensure filtration of a known sample amount, expressed in absolute terms (that is with a volume measure) or like percentage regarding the initial sample volume. The TTF value was evaluated during tests performed to calculate SRF and was the time needed to filter 50% of the initial sample volume.

Chemical and microbiological analysis on sludge and on effluent samples were performed according to the standard methods [19], IRSA–CNR methods [20] and Madoni's methods [21].

2.3. Experiments sets

Four different sets of experiments were performed: MBRcrs in normal condition; MBRcrs diluted to typical aerobic CAS sludge concentration (4–5 g_{TSS} l^{-1}); MBRcrs thickened for 24 h; MBRcrs conditioned with polyelectrolyte and ferric chloride in different concentrations and combinations. To ensure accurate and precise results, each experiment was repeated at least ten times because of the uncertainties, mentioned above, related to timing the test stop; so more than 270 tests were performed and evaluated.

2.4. Sludge conditioning

Sludge conditioning was performed according to IRSA–CNR methods [20] which reproduce the conditions of a full scale sludge treatment plant. These procedures establish that the amount of conditioning substance is function of TSS concentration and 20 ml of conditioning must be added for every 100 ml of sludge; so in case of combinations of polyelectrolyte and ferric chloride, 10 ml of each have to be added. Sludge is intensely stirred (120 rpm) for 5 min in a vessel with the conditioning solution, followed by slow mixing (45–60 rpm) for 10 min to avoid sludge flocs sedimentation. In the study mixing was performed with a jar test.

2.5. Materials

Polyelectrolyte and ferric chloride were added to the sludge as solution made before starting the test and stored maximum for 4 d. The polyelectrolyte used was Policat 914, a middle cationic charge polyelectrolyte. The ferric chloride and polyelectrolyte concentrations used were respectively 3%, 5%, 7%, 15%, 30% of TSS and 0.2%, 0.5%, 1% of TSS.

3. Results and discussion

3.1. MBR effluent quality

The pilot plant, treating a synthetic influent with a composition similar to domestic wastewater and contaminated by a concentration of 10 mg l^{-1} of total chromium, used in tannery industries, reached steady state condition one month. later being contaminated by the heavy metal. In fact chemical and microbiological analysis performed on the sludge and on the effluent samples showed stability in the effluent quality, in the TSS and in the VSS concentrations and in sludge floc microbiological composition [16].

The plant effluent quality was always good for reuse (EU Water Framework Directive 91/271/EEC) and fouling did not increase in presence of chromium. The metal produced insoluble compounds, such as chrome phosphate or chrome sulphate, and its total concentration increased in the sludge until 1000–1110 mg l^{-1} when steady state conditions were reached. It was mainly trivalent chromium while the hexa-valent one was always between 0.9 and 1 mg l^{-1}. The heavy metal concentration in the effluent was constantly below the detection limit of the atomic absorption spectroscopy (0.005 mg l^{-1}).

3.2. MBRcrs dewaterability tests without conditioning

The MBRcrs was collected from the MBR aerobic reactor and only when the pilot plant was stable, i. e. a steady state was reached. TSS average value was 11.77 kg m^{-3} and VSS 7.69 kg m^{-3}, where TSS are higher than Table 1 value, because chromium produced insoluble compounds that accumulated in the reactor due to the membrane and the high SRT. Meanwhile VSS value did not change when the influent was contaminated by chromium.

Results for the three sets of experiments without conditioning are visible in Table 2. MBRcrs SRF in normal condition was $2.58 \cdot 10^{11}$ m kg^{-1}; the SRF values for CAS are, usually, in the range 10^{12}–10^{14} m kg^{-1}. This clearly points out that MBRcrt has better dewaterability than CAS and it does not require mandatory conditioning before dewatering processes because SRF value is $< 10^{12}$ m kg^{-1} [20,22]. This is probably due to two reasons: SRT higher than 25 d for MBR plants produces stability in sludge unlike CAS plants; differences about the floc size, species composition and distribution of microfauna between CAS and MBR with chromium sludge [16]. Both reasons lead up to a higher quantitative of free water for MBRcrs than CAS sludge and the consequence is greater dewaterability.

The MBRcrs SRF in normal condition values have the same order of magnitude as those found for MBR sludge from municipal wastewater treatment plant with similar SRT [13] and much lower values than those (around 10^{15} m kg^{-1}) previously reported for MBR [14]; so chromium does not influence negatively the MBR sludge dewaterability.

As expected the sludge thickening produced better dewaterability condition but not really considerable, the SRF value decrease was only 8%; this is probably due to natural flocculation phenomena that take place in sludge during the thickening process. Instead the tests were 47% slower than normal condition, so natural flocculation changes the ratio between free and tied water, increasing sludge dewaterability, but produces a slower process. On the contrary, dilution effects were absolutely negative; even if dewatering was faster, yield was scarce because the amount of free water was too high.

3.3. MBRcrs dewaterability tests with conditioning

Results for experiments with conditioning are visible in Table 3 and looking at Table 3 values, it is possible to say that the conditioning experiments, both with polyelectrolyte and ferric chloride in all combinations of concentrations, did not improve MBR chromium rich sludge dewaterability. Instead, some tests with only polyelectrolyte or ferric chloride produced good results. In fact, increasing the polyelectrolyte concentration, the SRF percentage reduction decreased, from 45% to 16% for the polyelectrolyte concentration of a 0.2% of TSS and 1% of TSS, respectively. The behavior of the ferric chloride, instead, vacillated: with 3% of TSS, SRF decreased by 11%; with 5% of TSS, SRF decreased by 44%; with 7% of TSS, SRF increased by 46%; with 15% of TSS, SRF decreased by 22%; finally, with 30% of TSS, SRF increased by 16%.

The polyelectrolyte negative effect on sludge dewatering, when its concentration increased, was, probably due to an excess of free conditioning that, increasing the solution viscosity, produced less dewaterable sludge. In such situation the step of slow mixing has to last for more than ten min; in this way the excess of polyelectrolyte can react with the colloids, producing flocs with greater mechanical resistance.

The ferric chloride behavior was due to the destabilised ability of the ferric chloride on the sludge suspension: some concentrations favored attractive forces against repulsive and consequently aggregation between particles; other concentrations, instead, caused the reversal of the colloids superficial charge sign, producing a newly stable sludge suspension. Based on these interpretations, ferric chloride in the range 3–5% of TSS destabilized more effectively sludge suspension; with 7% of TSS a reversal of the charges sign and, therefore, a new stable sludge suspension occurred; increasing ferric chloride concentration, destabilization occurred again.

The combination of polyelectrolyte and ferric chloride did not improve sludge dewaterability, probably because of interaction between colloids and electrolyte in the solution. For low polyelectrolyte concentration, there are not enough electrolytes for colloids neutralisation and adsorption. High concentrations of ferric chloride could help sludge suspension destabilisation and improve flocs formation. Vice versa, for higher concentration of polyelectrolyte, the ferric chloride, neutralising the particles, limits the colloids number available for bridging by means of polyelectrolyte. In this

Table 2
Dewaterability characteristic for MBRcrs in normal condition, MBRcrs thickened and MBRcrs diluted

MBRcrs	TSS kg m^{-3}	VSS kg m^{-3}	VSS/TSS %	SRF m kg^{-1}		SRF variation %	TTF, 50% s		TTF, 50% variation %
				Average	St. Dev.		Average	St. Dev.	
Normal condition	11.97	7.69	64.35	2.58E+11	1.45E+10		17	3.3	
Thickened	20.97	13.51	64.43	2.38E+11	3.33E+10	–8	25	3.6	47
Diluted	5.20	3.37	64.81	5.17E+11	5.41E+10	100	11	2.8	–35

Table 3
Dewaterability characteristic for MBRcrs with conditioning

MBRcrs	Polyelectrolyte % TSS	$FeCl_3$ % VSS	SRF m kg^{-1}		TTF, 50% s		TTF, 50% variation %
			Average	St. Dev.	Average	St. Dev.	
Normal condition			2.58E+11	1.45E+10	17	3.3	
	0.2		1.42E+11	1.92E+10	7	1	–59
	0.5		1.54E+11	3.55E+10	9	2.6	–47
	1		2.16E+11	6.39E+10	23	7.5	35
		5	1.44E+11	2.06E+10	14	2.6	–18
		15	2.01E+11	2.97E+10	16	2.2	–6
		30	3.00E+11	2.74E+10	17	3.6	0
	0.2	5	5.41E+11	1.57E+12	42	22	147
	0.2	15	3.99E+11	8.58E+10	55	12	224
	0.2	30	4.51E+11	1.44E+11	52	13	206
	0.5	5	1.26E+12	6.62E+11	112	30	559
	0.5	15	1.09E+12	1.69E+11	92	8.7	441
Conditioned	0.5	30	7.90E+11	2.90E+11	97	16	471
	1	5	3.16E+12	8.92E+11	294	64.5	1629
	1	15	2.49E+12	9.35E+11	196	33.5	1053
	1	30	3.74E+12	1.29E+12	290	48.7	1606
		3	2.30E+11	6.79E+10	17	2.1	0
		7	3.77E+11	8.76E+10	28	3.6	65
	0.2	3	3.12E+12	4.8E+11	184	28.2	982
	0.5	3	3.15E+12	1.04E+12	238	63.1	1300
	1	3	3.35E+12	1.48E+12	251	65.9	1376
	0.2	7	2.61E+12	6.19E+11	160	29.8	841
	0.5	7	4.49E+12	1.05E+12	213	18.2	1153
	1	7	6.19E+12	4.82E+11	317	15.1	1765

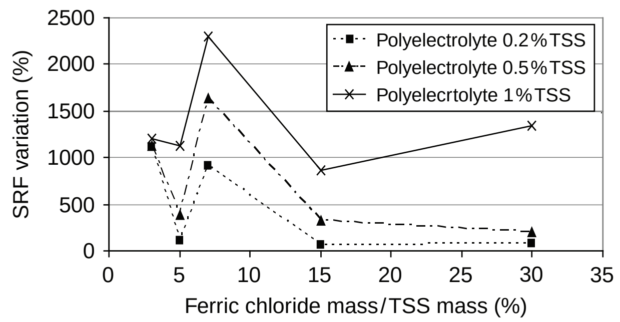

Fig. 1. SRF variation of MBRcs due to conditioning: ferric chloride influence.

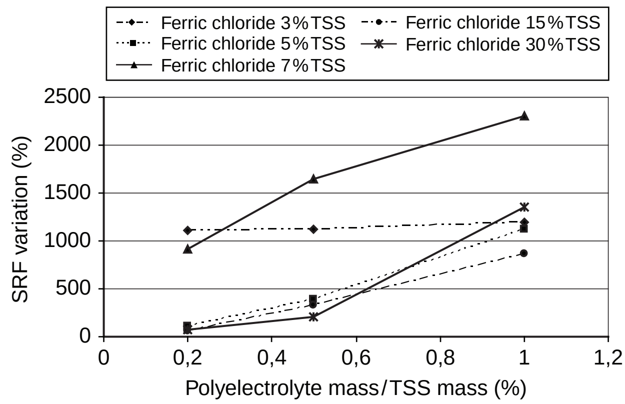

Fig. 2. SRF variation of MBRcs due to conditioning: polyelectrolyte influence.

situation free polyelectrolyte could increase the solution viscos ity or produce flocs high water concentrated. Both these eventualities concur to get sludge dewaterability worse.

SRF variation of MBRcs, visible in Table 3, due to conditioning with ferric chloride and based on the polyelectrolyte concentration, is plotted in Fig. 1. The tendency is for a SRF percentage increase reduction, with the exception of the combinations with ferric chloride in the concentration of 7% of TSS due to the reasons above explained. Moreover, Figs. 1 and 2 show that the worst combinations are all those with concentration of polyelectrolyte of 1% of TSS and ferric chloride of 7% of TSS.

The TTF and TTF variation values of Table 3 have a trend similar to SRF ones and therefore the comments above are valid for them; they show only absolute values variation smaller than SRF ones.

4. Conclusions

Specific Resistance to Filtration and Time To Filter were evaluated to characterise MBR chromium rich sludge dewaterability. The results point out that a treatment plant simpler than CAS is reasonable to design for MBRcrs, which reduce sludge treatment and disposal costs: thickening is not so useful as for CAS sludge (SRF value decrease was only 8% and tests were 47% slower than normal condition); a stabilisation step is not needed because MBR plants do not have a first clarifier and biological sludge is stable (SRT > 25–30 d); dewatering phase does not require a mandatory conditioning step due to its stability and floc structure (SRF for MBRcrs in normal condition was $2.58 \cdot 10^{11}$ m kg^{-1} that is $< 10^{12}$ m kg^{-1}) and even because sludge conditioning with a combination of both polyelectrolyte and ferric chloride does not increase sludge dewaterability. Instead, concentrations of polyelectrolyte of 0.2% of TSS or ferric chloride of 5% of TSS are useful, with a preference for the former condition. This, in fact, avoids the weight increment determined by ferric chloride utilisation, and the consequent increase of disposal costs.

Finally, the plant effluent quality was always good for reuse, fouling did not increase in presence of chromium and the heavy metal concentration in the effluent was constantly below 0.005 mg l^{-1}.

In conclusion, it is possible to affirm that the MBR plant with flat sheet membrane could treat wastewater contaminated by heavy metals without problems of bad effluent quality and promote MBR systems as an effective and efficient solution for tannery wastewater treatment.

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