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Chemically enhanced membrane process–towards a novel sewage treatment concept to potentially replace biological processes

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ABSTRACT

This study tested the potential of a chemically enhanced membrane process as a novel treatment system producing reusable effluent from domestic wastewater and potentially replacing biological treatment. The process involved chemical conditioning followed by a sequence of ultrafiltration and nanofiltration. Polyaluminum chloride (PACs) was selected as the optimum chemical reducing chemical oxygen demand (COD) in the supernatant to 80–100 mg/L, below the soluble COD level of 170 mg/L in domestic wastewater. Particle size distribution (PSD) analysis indicated that chemical conditioning removed 40–45% of the soluble COD fraction below 2 nm and modified the size distribution of residual COD below 450 nm, suitable for the following membrane treatment. Performance of the selected coagulant was also compared with $FeCl_3$. PSD results were also confirmed by batch experiments indicating that the proposed novel process was capable of generating a clear effluent with a COD of around 60 mg/L with micro/ultrafiltration and 35 mg/L with nanofiltration. The process offered the possibility of conserving more than 90% of the available energy in domestic wastewater, through both chemical conditioning/settling and entrapment by the membrane, which may be reused and/or recovered as part of sludge processing and disposal. The use of PACs was also observed to avoid bulky sludge generation associated with conventional chemical treatment.

Keywords: Enhanced membrane process; Wastewater treatment; Chemical conditioning; Particle size distribution; Ultrafiltration; Nanofiltration

1. Introduction

Biological treatment is now considered as the prescribed method of organic carbon removal from sewage. It mostly relies on a century-old activated sludge technology, where removal performance largely depends on gravity settling of biomass. Therefore, system design and operation are primarily focused on effective flocculent settling, often resulting in oversized aeration tanks [1]. Membrane bioreactor (MBR)

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has been a major achievement, which removed all constraints associated with gravity settling. However, it still suffers from operational problems mostly related to soluble microbial products, extracellular polymeric substances, etc., attributed to the metabolic activities taking place in the biological reactor [2,3]. At this stage, innovative research should address the following basic questions: Should biological treatment remain to be as the only viable option to ensure that the level of organic carbon (COD) in the effluent complies with effluent limitations? Can membrane technology be properly used to exclude biological treatment? This issue constituted the focal point of the study, which essentially explored the possibility of substituting biological treatment with a membrane filtration scheme after appropriate chemical conditioning of sewage, i.e. the chemically enhanced membrane process (CEMP), with an equal or better removal potential of organic carbon.

Adoption of the chemical oxygen demand (COD) as a representative parameter for substrate has been a major milestone in evaluating the fate of organics in wastewater. The study essentially requires a full understanding of the particle size distribution (PSD) of COD fractions in sewage mainly (i) to assess the role of chemical conditioning in tampering and improving PSD for membrane filtration and this way, (ii) to ensure the compatibility of CEMP as a sustainable treatment process. Thus, understanding the role of chemical conditioning should relate to the concept of particle size in wastewaters. In conventional wastewater characterization, the only size implication is the filtration size of 450 nm, which is used for arbitrary differentiation of particulate fractions from "soluble" component. This size threshold is also used for defining suspended solids and it is adopted as a basis for COD fractionation in current models [4]. Historically, a number of earlier studies on the subject attempted to differentiate and group organic matter in different size fractions, presumably with different biodegradation characteristics [5,6]. In recent years, PSD analysis has been introduced as a useful instrument for identifying fractions of COD and other significant pollutants in a much wider size range between 2 and 1,600 nm [7–9]. In this context, PSD analysis was mainly used in this study to visualize the impact of chemical conditioning on the expected efficiency of membrane filtration using different types of filters.

While significant improvements were reported in the removal of particulate matter (total suspended solids) and organic carbon (BOD_5, COD) by the addition of conventional coagulants and flocculants such as iron salts, alum, lime, and anionic polymers [10,11], the process could not survive the competition of biological treatment after 1940, mainly because it failed to produce a stable effluent with complete removal of biodegradable organic matter; it was also relatively expensive and generated large quantities of sludge. Attempts to promote process modifications such as Laughlin process or Guggenheim process that would completely stabilize and purify sewage could not also establish themselves as viable treatment alternatives [12].

Reviving chemical conditioning as part of an integrated wastewater treatment scheme has now become a viable option in the light of fundamental achievements in wastewater management, namely (i) recent developments and emerging technologies such as membrane technologies, and (ii) changes in conceptual understanding of sustainability which now regards waste as a resource. In fact, membrane technology has been a major breakthrough in wastewater treatment and reclamation for reuse: low-pressure membranes (usually MF or UF membranes) are currently being used as a tertiary/advanced treatment step following secondary clarifiers for the removal of suspended solids, human pathogens, and specific pollutants [2]. Similarly, membrane bioreactors reshaped conventional biological treatment as a novel process scheme by removing and replacing gravity settling. This was essentially the basis for envisaging the CEMP as a novel wastewater treatment scheme. The process was designed to involve a coagulation, flocculation, and settling sequence followed by membrane filtration, where the initial chemical conditioning phase would entrap and separate particulate and colloidal matter as well as a fraction of the soluble organics in a way to generate a modified size distribution much more suitable for membrane filtration. It relied on using low doses of new synthetic coagulants eliminating the problem of excessive sludge production. It also offered the possibility of full energy recovery from wastewater, conserving the bulk of chemical energy (COD) in the sludge, which would be consumed in conventional biological treatment at the expense of additional energy (aeration) input.

In this context, the objective of the study was to explore the potential of CEMP as a novel treatment system for domestic wastewater. The study was basically designed to test the limits of enhanced membrane operation for the removal of organic carbon in a way to generate an effluent suitable for recovery and reuse, mainly for irrigation. Specifically, it investigated the effect of chemical conditioning on the efficiency of membrane separation and evaluated sludge generation with related energy implications as given in the evaluation section.

2. Materials and methods

2.1. Experimental design

The adopted approach relied on lab-scale experiments testing the performance of selected process configuration involving a sequence of coagulation, flocculation, and settling as a chemical polishing/conditioning step followed by membrane filtration. They were conducted on domestic wastewater. Four samples were used as 6-h composites collected with 2-h intervals from the effluent of the grid removal unit of a municipal treatment plant in Istanbul, within a period of eight months. PSD analysis for COD and total organic carbon (TOC) was conducted on collected samples together with conventional characterization.

Chemical conditioning involved standard jar test experiments to identify the optimum dosage of a number of coagulants yielding efficient COD removal. Synthetic coagulants were tested at low concentrations for this purpose to avoid excessive sludge generation together with ferric chloride, a conventional coagulant mainly serving the purpose of comparison. Jar test experiments were repeated on a different wastewater sample using the selected coagulant and ferric chloride. PSD analysis was also conducted on the residual COD and TOC of the supernatants, mainly (i) to observe changes inflicted on corresponding PSDs by chemical conditioning, and (ii) to assess the performance of membrane filtration based on different membranes and filtration sizes. Performance results were confirmed with batch filtration tests for ultrafiltration and nanofiltration systems.

2.2. Coagulation and flocculation tests

The sequence of coagulation and flocculation was performed following the jar test method to determine the optimum concentration of coagulant to be added to wastewater. The stirring machine used for the test was a six-paddle jar tester (Scientifica FC6S model). During the test, wastewater sample with a volume of 1,000 mL was added to the beakers and stirred for 1 min at a speed of 120 rpm for coagulation, and for 30 min at a speed of 45 rpm for efficient flocculation. Then, samples were allowed to settle for 30 min. After sedimentation, the sludge volume was recorded and the supernatant was collected for further characterization. It should be noted in practice, coarse filtration may replace sedimentation depending on expected improvements in the efficiency of the process.

A preliminary study was conducted using potential coagulants for domestic wastewater. Selected coagulants were PACs (Rapidfloc-1223), and Ultrion 71230, Ultrion 71225, Nalco 71260, Nalco 71975, and Nalcolyte 7135, which were supplied from Nalco Company together with $FeCl_3$. Synthetic flocculants in anionic (WET-Treat® 7053 from Nalco Company) and cationic (WET-Treat® 7012 from Nalco Company) character were also used with selected coagulants.

In this study, a number of experiments have been carried out for the determination of optimum dosage of coagulants. The jar test experiments were designed for using all coagulants alone and with anionic or cationic flocculants. The flocculent dosage was kept as 0.1% (weight/volume, w/v) for all cases. Based on the results of the preliminary study, additional jar tests were performed using selected coagulants and flocculent at optimum dosage and a dosage lower than optimum, and supernatants were subjected to PSD procedure.

2.3. Particle size distribution

In this study, PSD analysis was only applied to raw wastewater and supernatants of the *jar test* experiments conducted with selected coagulants and dosages (100 and 250 mg/L $FeCl_3$, and 0.1 and 0.5 mL of PACs). PSD was determined by sequential filtration/ultrafiltration and measurement of particle sizes by laser diffraction.

The sequential filtration/ultrafiltration procedure was performed in a continuously stirred cell with a total volume of 400 mL (Millipore, Amicon 8400) as described by Dogruel et al. [9]. Initially, AP40 (1,600 nm), HV (450 nm), and GV (220 nm) filters were used sequentially for filtration. Permeates from 220 nm were subjected further to ultrafiltration and filtered sequentially from 13-, 8-, 5-, 3-, and 2-nm filters. Permeates of all filtration tests were analyzed for measuring corresponding COD concentrations.

Furthermore, particle sizes of wet samples were determined by Malvern Mastersizer 2000® (Malvern Instruments Ltd, UK) which measures particle sizes from 0.1 μm up to 1,000 μm by laser diffraction.

2.4. Membrane filtration tests

Treatability study was performed to evaluate the overall effectiveness of membrane filtration to treat domestic wastewater. A dead-end filtration unit (Sterlitech Marka HP4750) with a diameter of 49 mm and a membrane active area of 14.6 cm^2 was used for the experiment. The flow was forced through the membrane by pressurized nitrogen gas. Internal pressure was set at 0–60 bar by a digital manometer. Cross-flow filtration was provided by maintaining a constant

turbulent flow along the membrane using a magnetic stirrer surface to avoid accumulation of matter on the membrane surface. Flux was monitored via online monitoring of filtrate weight every one minute. Then, the pressure in the experimental filtration unit was released by using a valve. For the study, two types of membranes (a cellulose-UC membrane with molecular weight cut-off of 10 kDa and a NF-90 nanofiltration membrane) were used for ultrafiltration and nanofiltration. Membranes were studied at a constant operating pressure of 2 bar for ultrafiltration and 30 bar for nanofiltration at ambient temperature.

2.5. Analytical procedures

The COD parameter was analyzed based on the ISO 6060 procedure [13]. Total Kjeldahl nitrogen (TKN), NH_4-N, total phosphate (TP), MLSS, and MLVSS were analyzed in accordance with standard methods [14]. TOC analyses were carried out on a Shimadzu VCPN model carbon analyzer. The pH samples were measured with an Orion 720A+ pH meter. Orthophosphate analyses were carried out using Dionex ICS-1500 model ion chromatograph.

3. Experimental results and discussion

3.1. Wastewater characterization and PSD analysis

Studies were conducted on four different composite samples from the primary sedimentation inlet of one of the major treatment plants in Istanbul (Pasakoy WWTP), collected within a period of eight months in 2013–2014. Samples reflected no major changes in the general characteristics of sewage, which could be characterized with an average COD value of 450 mg/L; the average soluble fraction (SCOD) was 167 mg/L, corresponding to an SCOD/COD ratio of 37%, also quite typical of domestic wastewaters [10]. Analytical results also indicated that the average composition of the tested wastewater could be expressed in terms of 267 mg/L suspended solids (TSS), 180 mg/L volatile suspended solids (VSS), 75 mg/L TKN, and 6.0 mg/L TP. Table 1 outlines additional details of similar characterization surveys together with data for relevant characteristics of sewage at different locations in Istanbul reported in previous studies. Observed experimental results in the study basically reflected average strength sewage with respect to COD, with a typical SCOD/COD ratio, high in nitrogen and slightly low in phosphorus contents.

PSD analysis for COD and TOC were carried out by means of sequential filtration on two different wastewater samples. The results are summarized in Table 2. COD and TOC values measured in permeates after each filtration step were expressed as cumulative values, as they reflected the COD and TOC contents of the samples below the corresponding filter size. The first measurements yielded total COD and TOC levels in the samples, i.e. in raw sewage, as no quiescent settling was allowed before the PSD analysis, which provided physical separation of COD and TOC fractions into nine size intervals ranging from 1,600 nm down to 2 nm.

As shown in Table 2, the initial measurements indicated slightly different total COD values of 400 and 463 mg/L, both characterized with a COD/TOC ratio of 3.3. PSD analysis also defined dissolved organic carbon (DOC), a significant parameter for evaluating the compatibility of sludge for landfilling [20]. It should be noted that very few studies included SCOD and DOC monitoring in sewage: Dignac et al. [21] reported a

Table 1
Conventional characterization of domestic wastewater

	This study		Domestic wastewater (mean values) [15]		
Parameter	Mean	Range	Atakoy	Baltalimani	RCWP [16]
TCOD (mg/L)	455	400–485	450	353	90
SCOD (mg/L)	170	145–195	132	–	–
TOC (mg/L)	135	120–145	–	–	–
TSS (mg/L)	270	240–280	190	195	25
VSS (mg/L)	155	130–190	178	160	–
TKN (mg/L)	75	67–85	41	38	–
NH_3-N (mg/L)	54	45–60	27	23	–
TP (mg/L)	6.0	5.6–6.4	27	8.4	–
PO_4-P (mg/L)	3.8	3.5–4	–	–	–
pH	–	7.6–7.65	–	–	6–9

Table 2
PSD of the COD and TOC fractions for domestic wastewater

Separation technique	Particle size (nm)	This study				Dulekgurgen et al. [17]	Hocaoglu and Orhon [18]		Dogruel et al. [19]
		WW2		WW3			COD (mg/L)		
		COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	Gray water	Black water	COD (mg/L)
Total		400	121	463	140	440	370	1,010	1,190
Filtration									
Nylon net filter	11,000						228	740	
AP40 filter	1,600	168	46	218	66	155	223	390	360
HV filter	450	145	43	186	56	115	218	375	290
GV filter	220	131	42	167	51	85	210	360	260
Membrane filtration									
100 kDa	13	128	37	161	49	85	107	310	240
30 kDa	8	124	37	151	45	75	91	215	225
10 kDa	5	115	34	139	42	65	50	160	210
3 kDa	3	101	31	123	37	65	30	60	205
1 kDa	1	92	28	105	32	60	26	45	195

SCOD/DOC ratio of 3.64; in a survey at one of the largest treatment plants in Istanbul, SCOD and DOC were observed to vary between 220–275 mg/L and 72–80 mg/L, respectively, determined as fractions below 450 nm, corresponding to a SCOD/DOC ratio of 3.1 ± 0.25 [22]. The results in Table 2 define this ratio as 3.31–3.37, a range quite compatible with values provided in the literature.

Distribution of differential fractions in different size intervals normalized to the initial value defined a bimodal size distribution both for COD and TOC, where 53–58% (245–232 mg/L) accumulated above 1,600 nm, 23% (92–105 mg/L) below 1 nm, 9–11% between 220 and 1,600 nm, and the rest almost equally distributed between 1 and 220 nm. This information is quite significant as it sets the basis for evaluating the effect of chemical conditioning on PSD.

3.2. Chemical conditioning and settling

Five different synthetic coagulants were tested with and without polyelectrolyte addition on the same wastewater sample (WW-III) with a total COD of 450 mg/L, the same level as the average value of all samples analyzed. The soluble COD of the sample was 155 mg/L corresponding to 34% of the total COD. In two tests previously conducted without chemical addition/conditioning, a COD removal of 35–40% was achieved by plain settling, corresponding to a remaining COD range of 290–310 mg/L clearly above the SCOD threshold. Residual COD levels at optimum dosages after chemical settling are outlined in Table 3. Aside from PACs, lowest achievable COD concentrations were generally above 100 mg/L, remaining in the range of 95–138 mg/L. Only, conditioning with Nalcolyte 7135 did not prove successful as the final COD remained above 270 mg/L under best experimental conditions. While COD removals were lower as compared to $FeCl_3$, all observed COD levels after chemical conditioning and settling were below the soluble COD fraction of 155 mg/L in the wastewater sample tested, conventionally determined by filtration through 450-nm filter.

PACs application was by far the most efficient coagulation tested with synthetic coagulants, in terms of COD removals achieved. They were conducted on the same wastewater sample (WWI) used for $FeCl_3$ experiments mainly conducted for comparison, with PACs dosages varying in the range of 0.1–1.2. As illustrated in Fig. 1, chemical conditioning yielded a settled COD of 80 mg/L with 0.7 mL of PACs alone and slightly higher levels of 93 and 95 mg/L when the PACs dose was decreased to 0.6 and 0.5 mL, respectively. Slightly higher results were obtained using PACs with cationic PE at the same doses. When PACs was used together with the anionic PE, the residual COD was measured as 147 mg/L at 0.1 mL and 110 mg/L when the PACs was increased to 0.5 mL,

Table 3
Residual COD levels achieved with synthetic coagulants

Coagulant type	Optimum dose (mL)	Settled COD (mg/L)
PACs	0.7	80
PACs + anionic PE	0.5	110
PACs + cationic PE	0.8	92
ULTRION 71225	0.6	121
ULTRION 71225 + anionic PE	0.4	130
ULTRION 71225 + cationic PE	0.6	95
ULTRION 71230	0.6	104
ULTRION 71230 + anionic PE	0.6	107
ULTRION 71230 + cationic PE	0.6	111
NALCO 71260	0.4	109
NALCO 71260 + anionic PE	0.6	117
NALCO 71260 + cationic PE	0.8	175
NALCO 71975	0.6	138
NALCO 71975 + anionic PE	0.6	138
NALCO 71975 + cationic PE	0.6	138

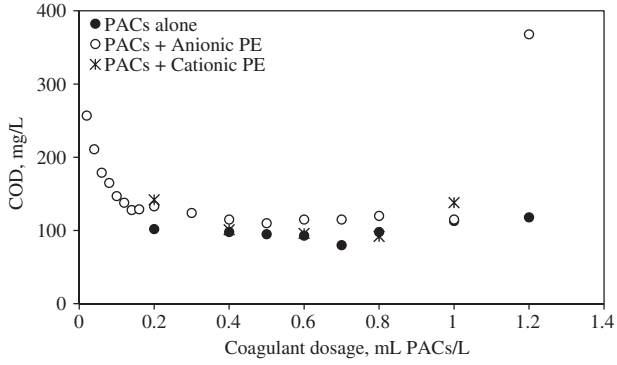


Fig. 1. Effect of PACs on COD removal with chemical settling.

with a much condensed and better settling sludge at all the tested doses. The experiments were also repeated on the wastewater sample WW-III together with other synthetic coagulants, yielding slightly lower results, where the residual COD could be reduced to 110 mg/L at 0.1 mL.

Chemical conditioning experiments also included ferric chloride ($FeCl_3$), a conventional coagulant used both in water and wastewater treatment. As will be elaborated in the following sections, $FeCl_3$ would be selected because of the bulky/chemical sludge that would be generated; thus, related experiments were designed essentially to show that a similar performance could also be achieved with the selected synthetic coagulant. In this context, the effect of $FeCl_3$ dose was tested in the range of 25–500 mg/L. Experiments were carried out in triplicate: In the first set, $FeCl_3$ was used alone and in the next two with the addition of 0.1% anionic or cationic polyelectrolytes (PE) selected for the study, using a wastewater sample (WW-I) with a total COD of 485 mg/L and SCOD of 195 mg/L.

In the coagulation/flocculation tests using $FeCl_3$ alone, a COD concentration of 103 mg/L could be obtained in the supernatant after settling with a $FeCl_3$ dose of 250 mg/L. Addition of 0.1% cationic polyelectrolyte did not improve the result, as the lowest observed COD level was 119 at 100 mg/L $FeCl_3$ + cat. PE. As shown in Fig. 2, the best COD removal efficiency was achieved in tests conducted with the addition of 0.1% anionic PE, where the remaining COD in the supernatant was lowered to 110 mg/L at 100 mg/L $FeCl_3$, to 80 mg/L at 250 mg $FeCl_3$, and finally to 72 mg/L at 300 mg/L $FeCl_3$.

Chemical settling tests were repeated on another wastewater sample (WW-II) with a COD of 400 mg/L and a SCOD of 145 mg/L, only using 250 mg/L $FeCl_3$ and 100 mg/L $FeCl_3$ + anionic PE, selected as optimum doses in the first set of experiments. Slightly higher COD levels of 103 and 131 mg/L were observed, respectively, in the supernatant after chemical settling.

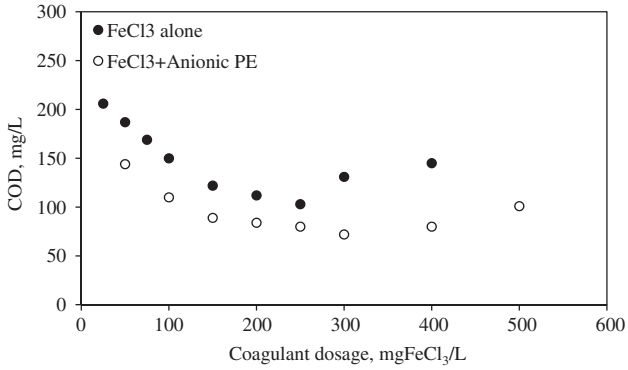


Fig. 2. Effect of $FeCl_3$ on COD removal with chemical settling.

The results indicated that a COD removal efficiency of 75–85% could be obtained with settling after chemical conditioning with appropriate doses of $FeCl_3$. Aiyuk et al. [23] found similar results (average total COD removal of 73%) from a CEPT pretreatment conducted by the addition of $FeCl_3$ as a coagulant and anionic organic flocculant. They are in agreement with the observations of a similar study in Istanbul on the *Yenikapi* discharge, with a significantly higher COD content of 825 mg/L due to industrial activities in the collection zone. In that study, the $FeCl_3$ dosage was changed in the range of 50–300 mg/L, together with a polymer addition of 2 mg/L (Separan-AP30E); the optimum $FeCL_3$ dosage remained between 150 and 200 mg/L, also yielding a COD removal rate of 85% [24].

At this stage, three observations deserve additional emphasis regarding the outcome of chemical conditioning experiments: (i) the performance of PACs, selected as the optimum synthetic coagulant was quite comparable with that of $FeCl_3$ (ii) the remaining COD values of 80–110 mg/L after chemical settling remained significantly lower than the corresponding SCOD levels in the wastewater, so that a part of COD in sizes lower than 450 nm was also removed by entrapment, adsorption, and/or chemical binding. (iii) COD removals achieved by chemical settling, although significant, remained somewhat below the range generally obtained with biological treatment, justifying the need for membrane treatment as a polishing step after chemical conditioning.

3.3. PSD analysis

Wastewater samples, settled after chemical conditioning with PACs and $FeCl_3$ were additionally subjected to PSD analysis, which basically yielded specific size fingerprints for the residual COD. For this purpose, the sequence of flocculation and settling was repeated on another wastewater sample with two different doses of the selected coagulant, which provided best COD removal in the previously conducted similar tests and the supernatants were used in the PSD experiments.

PSD analysis was first performed using 0.5 mL of PACs and 0.1 mL of PACs + anionic PE, selected as optimum dosages in the previous experiments, on supernatants of chemical settling tests conducted on a different sewage sample with a COD of 450 mg/L and SCOD of 155 mg/L. The residual COD levels, measured as initial levels of PSD experiments, were 88 and 114 mg/L, respectively. The results listed in Table 4, exhibited a uniform size distribution both for

Table 4
PSD of COD after chemical settling with 0.1 and 0.5 mg/L PACs

		0.1 mL PACs		0.5 mL PACs	
Separation technique	Particle size (nm)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)
Total		114	36	88	28
Filtration					
AP40 filter	1,600	95	29	78	24
HV filter	450	91	28	73	22
GV filter	220	82	25	69	21
Membrane filtration					
100 kDa	13	77	23	69	20
30 kDa	8	73	22	54	16
10 kDa	5	68	21	40	12
3 kDa	3	64	19	33	10
1 kDa	1	64	19	33	10

COD and TOC; PSD analysis indicated a COD distribution significantly reduced down to 33 and 64 mg/L below 2 nm, respectively, significantly below the corresponding COD fractions of 93–105 mg/L in raw sewage (Table 2).

In the following experiments conducted on WW-II with $FeCl_3$, the selected dose was 250 mg/L when the coagulant was used alone and it was reduced to 100 mg/L when supplemented with 0.1% anionic polyelectrolyte. Resulting PSD profiles both for COD and TOC are summarized in Table 5. The application of 250 mg/L $FeCl_3$, which generated a COD level of 103 mg/L in the supernatant prior to the PSD test, proved to be more efficient as it could be reduced down to 29 mg/L through membrane filtration. In the parallel test started with an initial COD value of 131 mg/L, the final concentration was 51 mg/L below 1-nm size. It should also be noted that the COD/TOC ratio after chemical settling was 3.3, the same level as in the wastewater sample; this ratio did not appreciably change through membrane filtration.

In all chemical conditioning experiments performed with PACs and/or $FeCl_3$, the observed residual COD remained always below the corresponding SCOD level in the wastewater sample, clearly indicating that the coagulants were effective, in removing not only particulate components but also a part of COD fractions below 450 nm, the size threshold conventionally defining SCOD.

This aspect is better visualized in Fig. 3, which displays the results of PSD tests in terms of incremental size fractions of residual COD after chemical conditioning as compared with the corresponding size fractions in raw wastewater. As shown in Fig. 3(a), the peak at higher sizes was totally trimmed with PACs, which proved to be significantly more efficient in removing particulate COD; only one major COD peak remained below 2 nm, but also with a similar significant removal from 105 mg/L in raw wastewater down to 64 mg/L (39%) with 0.1 mL PACs + PE and to 33 mg/L (68%) with 0.5 mL PACs.

For $FeCl_3$, while the major removal was observed to occur at high sizes, Fig. 3(b) still shows a bimodal distribution with a remaining COD fraction of 21–34 mg/L above 1,600 nm. However, it also indicated a significant COD removal in the soluble range below 2 nm from 92 to 51 mg/L (44%) with 100 $FeCl_3$ + PE and further down to 29 mg/L with 250 mg/L $FeCl_3$. Random changes were measured in the size range of 2–220 nm.

Changes induced by the coagulation/flocculation sequence were also investigated for particles with higher sizes between 0.1 and 100 μm with *microsizer* analyses. In the raw wastewater, the particles were distributed between 0.48 and 832 μm with a volumetric median—i.e. the size that separates half the particle volume—value of 36 μm. The corresponding 10 percentile value—the particle size that differentiates 10% of particle volume in the lower size range—was calculated as 9.8 μm and the 90 percentile value as 178 μm. As shown in Fig. 4, the PSD was significantly skewed toward the larger sizes both for $FeCl_3$ and PACs as a result of coalescence of particles due to coagulation/flocculation processes, with higher median and 90 percentile particle size values. In fact, the distributions displayed in Fig. 4 yielded 151 and 350 μm as median and 90 percentile particle sizes for $FeCl_3$ and 211 and 475 μm for PACs, with a clear indication that PACs was also a more effective coagulant at larger particle sizes.

Table 5
PSD of COD after chemical settling with 100 and 250 mg/L $FeCl_3$

		100 mg/L $FeCl_3$		250 mg/L $FeCl_3$	
Separation technique	Particle size (nm)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)
Total		131	40	103	31
Filtration					
AP40 filter	1,600	97	30	82	25
HV filter	450	93	28	78	24
GV filter	220	89	27	73	22
Membrane filtration					
100 kDa	13	72	22	69	21
30 kDa	8	65	20	58	18
10 kDa	5	60	18	54	16
3 kDa	3	55	17	38	12
1 kDa	1	51	16	29	9

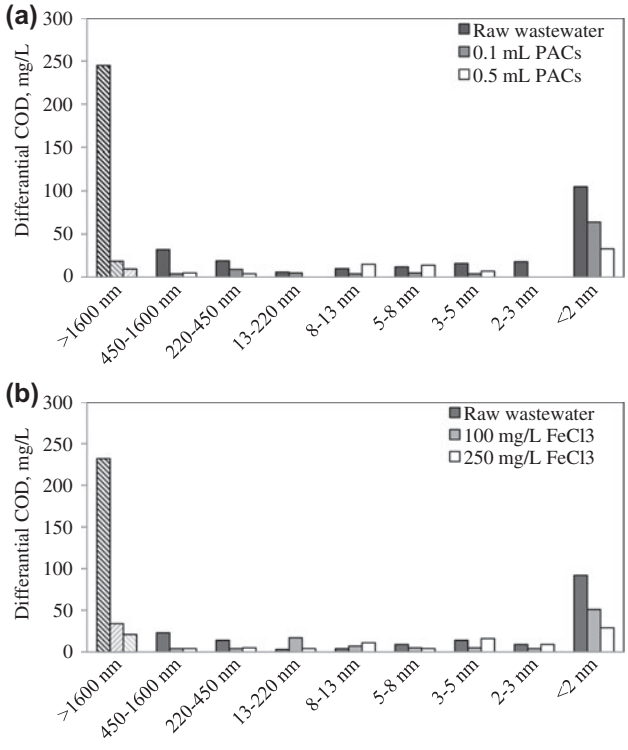


Fig. 3. Effect of chemical conditioning on incremental COD size distribution of (a) PACs and (b) $FeCl_3$.

3.4. Evaluation of results

A number of significant issues derived from the observed experimental results deserve additional emphasis, mainly to underline the scientific and technological merit of the tested CEMP, as a novel wastewater treatment system. First of all, PSD analyses defined a bimodal size distribution for sewage with two peaks, one in the particulate range and the other in the nanosize (1–2 nm) range. The sequence of coagulation and flocculation before settling proved to be effective, not only on the particulate COD fractions as traditionally conceived in wastewater treatment practice, but it significantly lowered the second peak in the soluble range. Interpreted in terms of PSD results, chemical conditioning induced a residual COD with a totally different size distribution fingerprint with a much lower fraction in the nanosize range, which significantly increased the removal potential of membrane filtration to be applied as the final polishing sequence. This aspect is better visualized by means of the cumulative size distribution profiles of residual COD obtained with chemical conditioning and settling. Fig. 5 displays these profiles obtained with optimum doses of PACs and $FeCl_3$ and together with ranges of microfiltration, ultrafiltration, and nanofiltration systems commercially available in the market. This way, it gives clear indication that microfiltration or ultrafiltration would potentially reduce the COD level in permeate below 70 mg/L. It should be noted that the expected efficiency of the two systems would be compatible as the incremental COD within the size ranges defining microfiltration and ultrafiltration applications appears to be quite low for the tested sewage characteristics. The same data show that nanofiltration offers the potential of reducing permeate COD below the 40–50 mg/L level. This level would be sometimes hardly attainable by means of conventional biological treatment under adverse conditions subject to particulate matter escape from secondary settlers and/or high concentrations of soluble residual microbial products in the effluent.

Indications of cumulative PSD profiles were confirmed by means of batch membrane filtration tests after chemical conditioning and settling with the selected optimum dose of 0.5 mL of PACs, conducted on a different sewage sample (WW-IV) characterized by 480 mg/L COD; 175 mg/L SCOD; 78 mgN/L TKN; 46 mg/L ammonia as N; 5.6 mg/L total-P and 4.5 mg/L PO_4-P as P. The tests yielded a treated effluent with a permeate COD of 62 ± 9 mg/L for the

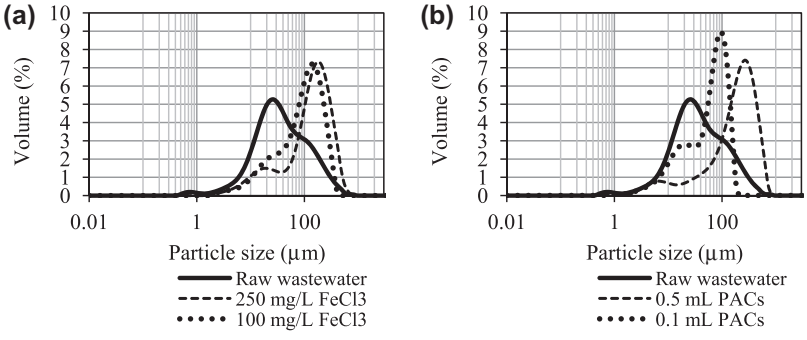


Fig. 4. Effect of chemical conditioning on larger particles by dosing (a) PACs and (b) $FeCl_3$.

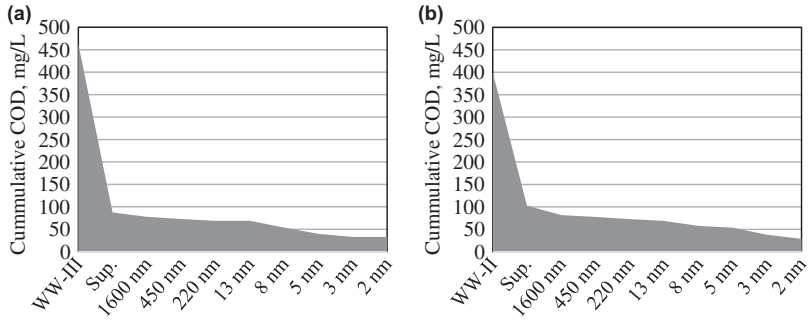
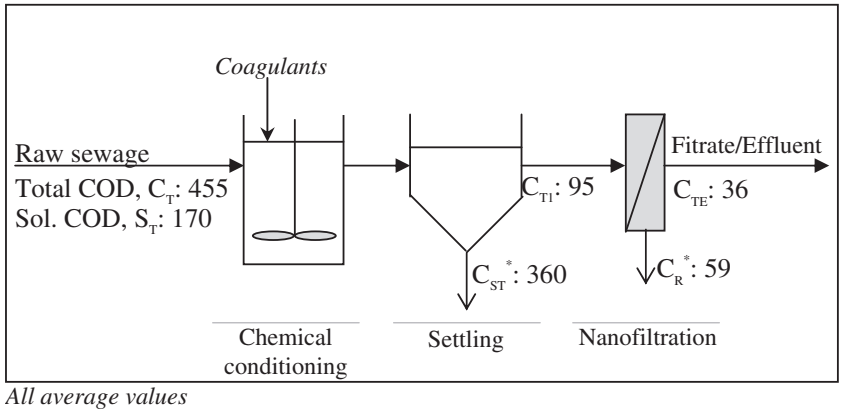


Fig. 5. Expected removal efficiency of membrane filtration based on chemical conditioning with (a) 0.5 mL PACs and (b) 250 mg/L $FeCl_3$ (Sup.: supernatant of chemically conditioned wastewater).

ultrafiltration unit using a Microdyne PSUH hollow fiber filter with a pore size of 100 kDa (13 nm), and 36 ± 5 mg/L for the nanofiltration unit using a Koch TFC spiral filter with a pore size of 3 kDA (2 nm) nm. Total phosphorus in the effluent was reduced down to 0.5 mgP/L and total nitrogen to 59 mgN/L, approximately to the ammonia nitrogen level in the raw sewage, regardless of the filtration type implemented, presumably as a result of chemical conditioning and settling. The basic structure and performance of the proposed chemically enhanced membrane filtration process as tested in the experiments are illustrated in Fig. 6. It should be noted that a number of options may be envisaged for the settling step prior to membrane filtration, such as gravity settling and course filtration trough filter press, etc.

Secondly, the potential of CEMP as a novel wastewater treatment system should also be evaluated in terms of resource/energy management. It is well known that domestic wastewater incorporates significant chemical energy approximately equivalent to 3,300 kcal/kg COD [25]. This corresponds to around 1,500 kcal/m^3 domestic wastewater tested in the study. Conventional biological treatment is designed and operated to overlook this potential energy, aiming to remove all available COD and to stabilize to the extent possible to generate biomass at the expense of significant aeration/energy input; in short, it requires and consumes additional energy for wasting all the available chemical energy in the wastewater. In contrast to traditional biological treatment, CEMP additionally offers the possibility of conserving more than 90% of the available energy, through both chemical conditioning/settling and entrapment by the membrane, which may be reused and/or recovered as part of sludge processing and disposal.

Finally, the process should also be evaluated based on advantages and merits of utilizing PACs as a synthetic coagulant as opposed to traditional coagulants such as $FeCl_3$. PACs usage makes chemical conditioning a viable option, mainly through significant reduction in sludge generation, historically identified as a



All average values
**mg per L of wastewater treated*

Fig. 6. Process performance and COD mass balance of chemically enhanced nanofiltration.

major drawback in practical applications. In fact, experiments indicated around 500 mg/L (0.5 kg/m^3) chemical sludge generated when using $FeCl_3$ as a coagulant, a level quite close to 490 mg/L theoretically calculated on the basis of chemical precipitation stoichiometry; in the experiments, the amount of sludge was observed to drop to around 350 mg/L (0.35 kg/m^3) limited with TSS and incremental COD settling only when using PACs, inducing a 30% decrease as compared to $FeCl_3$.

4. Conclusions

The results provided conclusive experimental support for setting the basis of CEMP, as an innovative treatment scheme for sewage. It showed that CEMP, when properly tailored, reflected the potential of replacing biological treatment, as a system with equal or better efficiency, with attributes to constitute a viable alternative for removing organic carbon from sewage and producing reusable effluent with optimum energy conservation.

It also underlined the role of PSD analysis both as an integral component of wastewater characterization and a prerequisite for selecting the proposed treatment scheme. The bimodal size distribution characterizing COD and TOC contents of domestic wastewater had a decisive impact on selecting the structure of the novel process. Chemical conditioning, not only reduced COD significantly below the soluble COD threshold in the wastewater, but also modified the PSD of the remaining COD in the supernatant. It is recommended that further studies be conducted on additional scientific and practical issues that would help to better establish the process for practical applications.

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