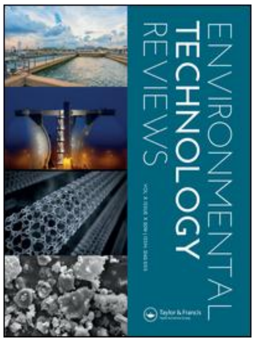

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Particle size distribution as an emerging tool for the analysis of wastewater

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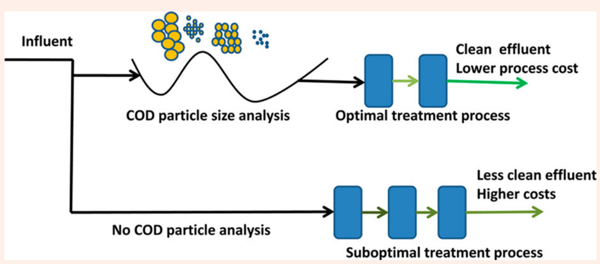
ABSTRACT
The technologies for analysis of wastewater contaminants have recently experienced rapid advancement. One of these technologies, with high potential in wastewater treatment is the analysis of the particle size distribution (PSD) of contaminants. However, there are no detailed documented studies on the application of this technique. This study aimed at critically reviewing the technologies for PSD analysis and the application of chemical oxygen demand (COD) fractionation analysis for the characterisation of municipal wastewaters. The suitability of the PSD technology for wastewater depends on the type of wastewater and its treatment process applied. Despite the advancements in PSD technologies, many researchers and industrialists are yet to utilise PSD analysis for wastewater. It is possible to use PSD to map out the foulants distribution for optimal design of membrane treatment of municipal and other wastewaters. Biological processes increase colloidal particles which are predominantly responsible for membrane fouling. There should be more investigations on how different wastewater treatment processes alter the PSD of contaminants. More usage of PSD analysis will lead to faster and more optimal designs of the treatment processes for the removal of contaminants. It will also have great usage in the process design for the recovery of useful products from the wastewaters.



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KEYWORDS
Particle; treatment; effluent; distribution; analysis

Terms

BOD Biochemical oxygen demand
COD Chemical oxygen demand
DOC Dissolved organic carbon
HMWF Heavy molecular weight fraction
HPLC High-performance liquid chromatography
HPSEC High-performance size exclusion chromatography
LC Liquid chromatography
LMWF Low molecular weight fraction
MBR Membrane bioreactor
MDW Molasses distillery wastewater
MP Microbial products
MW Molecular weight
MWCO Molecular weight cut-off
NF Nanofiltration
OCD Organic carbon detection
OMW Olive mill wastewater
PAC Powdered activated carbon
PES Polyethersulfone
POC Particulate organic carbon
PSD Particle size distribution
UF Ultrafiltration
SMP Soluble microbial products
TOC Total organic carbon
TN Total nitrogen
WW Wastewater

1. Introduction

The earliest debate on the characterization of impurities in wastewater was whether to use total organic carbon (TOC) or chemical oxygen demand (COD). Some researchers argued on the preference of the former because unlike the later, it is not affected by the oxidation state of the carbon [1]. However, the use of COD was eventually adopted due to its simplicity in analysis and is now more widely used compared to TOC. Later, it was discovered that the measurement of absolute chemical oxygen demand is not analytically sufficient in determining the pollutants in

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wastewater. It is possible for effluents with similar COD concentrations to have quite different characteristics due to a different distribution of the COD particles [2]. This implies that the mere characterization of organic pollutants in wastewater treatment plant influent by measuring their COD does not give sufficient understanding of wastewater qualities to design a good process. A wastewater rich in humic substances and another in sugars may have the same COD but their properties when treated by different technologies, remain far apart. Therefore, it is important that the characterisation of COD particles by size fractions and other properties beyond absolute total COD determination is done before developing the process for treatment of wastewater.

The wastewater load can be categorised according to size as; dissolved (<1 nm), colloidal (0.001um-1um), supracolloidal (1–100 µm) or settleable (>100 µm) [1,3] COD. This expanded scope of characterisation is widely used in activated sludge processes of municipal wastewater treatment. It is possible to further characterize COD according to the biodegradability of its size fractions. This categorization has created the basis for most modern models of activated sludge which can be adopted for other organic wastewaters. It is, however, important to note that the particle distribution in wastewater does not occur in discrete steps but occurs as a continuous increase of diameter. The power law was used to describe this continuous size distribution of contaminant particles in three biofilm treatment systems of municipal wastewater [4]. The parameters in the power equation were also correlated to other wastewater parameters like total COD, suspended solids and the turbidity [4].

The distribution of particles by size and other characteristics in the influent is not static but varies during the treatment process. The main cause of variation is the non-uniform elimination of COD as well as the production of other substances by microbes or breakdown of existing ones into different particles [5]. The substrate modification by added treatment chemicals also affects the PSD in wastewater treatment. The preferential reaction of added chemicals with certain COD particles also affects the PSD of COD in the substrate. Other factors that affect the PSD during wastewater treatment include the reactor used, substrate type and operating conditions like retention time [6]. In the event of integrated treatment processes, the process engineer should consider the possible modifications of the contaminants' fractional distribution caused by individual wastewater treatment processes during the process design.

There are several methods of characterisation of wastewater before the design of the treatment process. Some of the traditionally used parameters in wastewater analysis include COD, biochemical oxygen demand (BOD), pH, total dissolved and suspended solids, colour and nutrients. The use of PSD in the determination of the distribution of these parameters in various COD fractions would send more light during the design of the treatment process. There are also other emerging contaminants like microplastics, pharmaceutical compounds, heavy metals, phenolics, and other toxicants [7]. The tightening of effluent discharge standards by most environmental bodies necessitates further steps to eliminate these pollutants before effluent discharge. The use of PSD to determine their distribution in different COD fractions can help in the design of optimal treatment processes. In addition to determining the effectiveness of the effluent treatment method, the PSD can also be used to generate fingerprint data necessarily for preliminary selection of the treatment process for different wastewaters.

The study reviewed the technologies which are commonly applied to undertake PSD in wastewaters. The usage of the particle size distribution as an analytical tool for studying organic matter distribution in municipal effluents by various groups has been documented. In addition, the application of COD particle size and biodegradability distributions in the formulation of activated sludge models was studied. Moreover, the possibility of using the PSD of contaminants to map out the recalcitrants and foulants in wastewaters for the design of treatment processes was suggested.

2. Technologies for particle size distribution

The technologies for characterizing the particles based on their size have increased tremendously in recent years. The methods depend on various factors including; the sample quantity available, the size of particles to be analysed, analysing time limits, the accuracy required, number of samples to be tested and the cost of analysis. For small size particles like molecules, simple compounds, polysaccharides and proteins, gel filtration has been widely used in the past. Despite the requirement of a small sample, the process is cumbersome and time-consuming. Another traditional method of particle size analysis was sieving; which was used mainly for large particles. Centrifugation can also be applied to both particulate and colloidal particles in sample preparation. The usage of sieving is limited by high sample requirement and low accuracy.

2.1. Membranes as a tool for particle size characterization

Membrane separation is the most applied method of separating different COD fractions before analysis by other methods [8–10]. It is also possible to characterize the particles in wastewater with only membranes that are calibrated for various particle sizes [11]. In such applications, the COD fractions, separation may take the form of sequential filtration or parallel filtration. For a sequential process, the permeate stream from a large pore membrane unit becomes the feed for the following smaller pore size membrane unit. The COD retained in the membrane is added to that from previous filtration steps to calculate the COD which is greater than that of pore membrane used. In a parallel filtration process, similar samples from a uniform source are subjected to different pore sized membrane treatments. The difference in COD removed by the two membranes gives the mass of particles whose size range is represented by the two membranes. The latter method is less cumbersome and faster than the former. It is, however, more prone to errors because of the possibility of membrane pore blockages caused by high concentration of feed. Moreover, in parallel filtration, the formation of filter cake can block the pore membranes, therefore, causing the removal of particles smaller than the applied membrane cut off. This can create high errors in size fraction computation. Application of Membranes as stand-alone analysis process is limited by the requirement of a large quantity of the samples and much time compared to upcoming analysis technologies.

2.2. Other technologies for particle size analysis

The desire for greater accuracy, faster and convenient operations of particle analysis has resulted in the development of sophisticated technologies of particle size analysis. These include; plasma-mass spectrometry [12], LC-OCD [13], Transmission electron microscope [14], dynamic light scattering [14], flow field flow fractionation, hydrodynamic chromatography [12], Fourier transform infrared spectroscopy [15], Malvern counter [16] and Coulter-counter [17]. The applicability of various processes of analysis is dependent on several factors including; the size range of particles to be analysed, speed and the accuracy of the analysis required, and the sample quantity available. A summary of the size range of commonly used technologies for PSD analysis and their applicable particle size ranges is given in Figure 1. Most sophisticated technologies for analysis of COD distribution were not initially targeted to wastewater analysis. The demand for greater accuracy and faster operations has seen more of them get in these applications. New methods for analysing particulate COD like Coulter-counter method (size >0.8 µm), laser light scattering (size <100 µm), and steric field flow (<100 µm) have been used to analyse complex wastewaters like slaughterhouse wastewater and swine manure [18,19]. There are also reports of the use of NMR in the analysis of COD fractions in wastewater [20].

The new methods of analysing the distribution of COD fractions are based on scientific principles like; electrical resistance, resonance, light scattering or light blockage. The appropriateness of the technology for the analysis of PSD is dependent on characteristics of the target particles. For the huge suspended solids, the methods of separation from the rest are microfiltration, sieving, centrifugation, and sedimentation. The ultrafiltration and nanofiltration processes are used to separate fractions of different sizes from soluble COD. In addition to particle analysis, the main application of these methods is sample preparation for analysis by other more sophisticated methods. The pretreatment removes huge particles which may damage the analysis machines or cause errors in measurements. The presence of these huge particles can affect the analysis process for example with the light scattering instruments.

There are analysis technologies which are exclusively for the soluble COD analysis like LC-OCD, flow field fractionation, gel filtration chromatography, HPLC and SEC. The input sample to these processes should be well prepared to remove any particulate contaminants by methods like pre-filtration. One advantage of these methods is high precision and small sample requirements. Other technologies like Malvern counter, and steric flow fractionation can be used to quantify particles in both soluble and particulate fractions. The membrane filtration is commonly used to separate COD particles in both regions. The electrical impedance is used to quantify the particles in a fluid which acts as

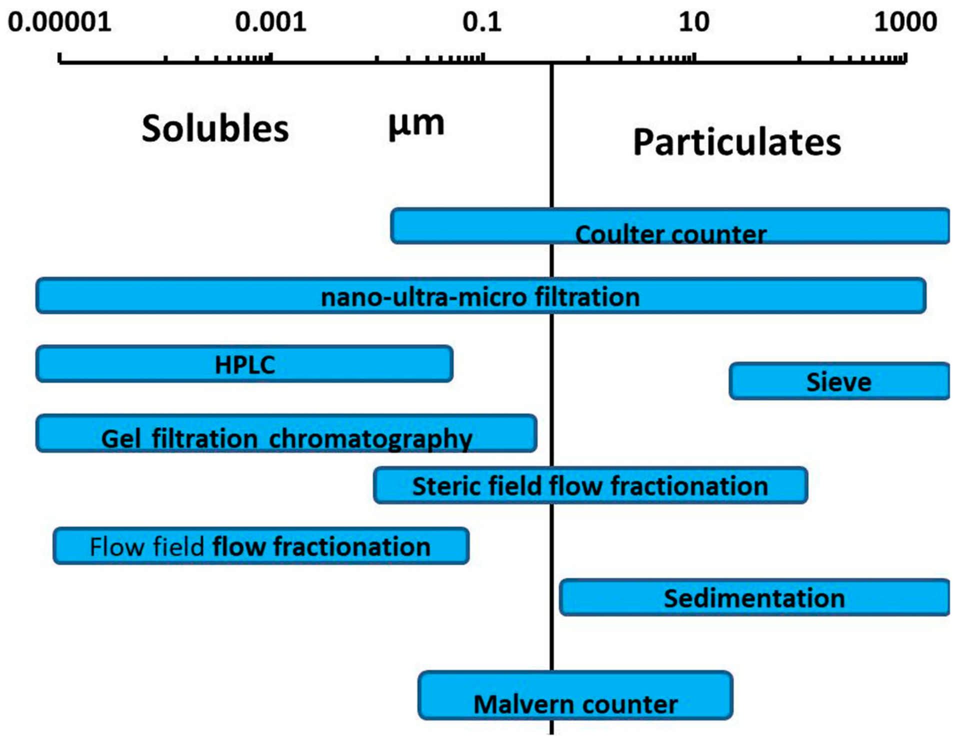

Figure 1. Usage range of PSD technologies.

an electrolyte. As the fluid passes through an orifice, the particles cause some impedance or resistance to current flow. The impedance of the particles causes voltage pulses which can be related to the mass of the particles. The main limitation to this technology is where the substrates contain particles that are of different nature, size and properties which make the correlation difficult. The Coulter counter is one of the PSD instruments employing the electrical impedance principle. The use of electrical resistance is disadvantaged by electronic noise while the interference by smaller particles or bubble could cause an error with the light scattering methods. The digital imaging principle is limited by the presence of dirt and colour in wastewater which necessitates the use of very high dilutions. The possibility of real-time analysis and simple operations are the main advantages of instruments using digital imaging and electrical resistance principle.

The resonance is another principle applied by PSD technologies. As the particles pass through a resonating cantlever, they cause some alteration of the resonance and this is quantified. The number of resonance alterations can also be quantified and correlated to give the number of particles. The Malvern counter is an example of equipments which use resonance principle [21]. In laser diffraction technology, the particles are made to pass across a beam of light in a certain direction. These particles diffract or scatter the light in a certain angle depending on the particle size [22]. The particle distribution is calculated by collecting all the diffracted beams and subjecting them to analysis program and the result displayed on a monitor. A related technology to laser light scattering is dynamic light scattering where the laser light intensity of diffracted beam by the particles in a solution is related to hydrodynamic radius. The diameter is then correlated to the particle diameter [23]. The summary of the technologies which are applied to characterize the COD particles is given in Table 1.

3. The use of PSD in the characterization of the municipal effluents

The particle size distribution (PSD) in wastewater treatment refers to the analysis of COD composition and the classification of COD particles into different size fractions. Its most common application is in the characterization of complex effluents. Some of the wastewaters which have their PSD analysis documented include Municipal wastewater, MDW, olive mill wastewater (OMW), tannery wastewater and textile wastewater. The analysis of the COD for such

Table 1. Technologies for PSD analysis.

Technology	Advantages	Disadvantages	Application	Wastewater analysed	Particle size range	reference
Resonance mass measurement	• Small sample • Easy to use • High particle concentration	• No uniform method for different particles	Malvern counter	Municipal activated sludge	1.2–600 µm	[16]
Electrolyte resistance	• Easy operation	• Highly conductive particles • Small particles behaving as one large particle	Coulter-counter multisizer	Agricultural WW, coagulation & flocculation treated	0.75–80 µm	[17]
			Electrical	Slaughterhouse effluent	0.01–10 µm	[18]
Sequential ultra/nanofiltration	• Inexpensive • Easy to use • Reliable	• Large sample • Charge effect • Only size range and not individual size separation	Filtration	OMW, Fenton treated	0.002–1.6 µm	[24]
			Filtration	Pulp & paper WW	0.003–8 µm	[8]
			Filtration	Municipal WW	0.01–100 µm	[25]
			Filtration	Textile dye WW	0.001–0.05 µm	[9]
Laser diffraction	• Small sample • Low conc. Sample • Fast and easy set up	• Multiple scattering	Diffraction Silas 1180L	Pig slurry	0.04–2200 µm	[19]
			Diffraction DLS	Pig manure	0.05–10 µm	[26]
			Diffraction Cilas 1180	Tannery effluent	0.01–100 µm	[27]
			Nanosizer	Olive vegetation WW	0.0008–6.5 µm	[28]
			Malvern Mastersizer2000 UK	Domestic wastewater	0.002–1.6 µm	[29]
			Accuser 780	Storm water	2–1000 µm	[30]
Particle image analysis	• Fast	• Interference • Coloured effluent • Small particles not detectable	Digital image analysis	Textile WW	5–180 µm	[31]
			LiQuilaz + model equation	Municipal WW	0.2–125 µm	[4]
High performance chromatography	• High resolution	• Expensive • Calibration • Maintenance	LC-OCD & Filtration	Domestic WW	0.026–1.2 µm	[32]
Size exclusion chromatography	Fast, easy	• Indeterminate peaks • Small output sample	SEC + Ultrafiltration	Anaerobic effluent	1–300 kDa	[6]

wastewaters by the method is meant to help in the design of appropriate processes for good treatment. This study has only looked in detail at the application of PSD in analysis and characterization of municipal wastewater. This wastewater is among the effluents which are most characterized by PSD method [3,33,34].

Municipal wastewater contains effluents from different sources including; domestic, industrial and agricultural wastewaters. It is composed of different types of compounds and COD particles. The process of its treatment encompasses various stages where the particles are removed or modified. A PSD study of municipal wastewater from different sources indicated that almost half of organic matter was in the soluble fraction for both primary and secondary effluents [35]. In this investigation, a similar pattern where the percentage COD in the primary and secondary effluent was almost equal was observed in every COD size fraction [35]. This implies a non-discriminatory removal of COD fractions by the treatment process. A separate study on municipal wastewater reported that the content of TOC was 50% total contaminants before primary treatment but reduced to 20% after digestion [34]. The same observed that a third of the TN in primary treatment was amino acids of which more than two-thirds were eliminated by the process [34]. In addition to primary and secondary sedimentation, the use of aeration tank is the most common method of treatment of municipal wastewater. Investigations on the changes in the wastewater composition after this treatment stage are thus necessary. One of the tertiary processes of treating municipal wastewater entails using various filtration treatments. It is therefore important to know forehand the COD removal by various membranes so that a good treatment regime can be designed. Another group used PSD and established that the mean diameter of particles of the activated sludge of municipal effluent was 25 µm [36]. In this study, most of COD was observed to be eliminated by 30 kDa ultrafiltration, whereas only 50% soluble COD was eliminated by 100 kDa microfiltration [36].

A separate PSD study on municipal effluent observed a two-fold decrease in particulate COD and an increase in percentage phosphorous after primary treatment [37]. This implies that the phosphorous nutrient had less preferential removal compared to other COD and therefore requires further treatment. In addition to conventional organic matter, the municipal wastewater contains other substances like pharmaceuticals [38], personal care products [39] and other toxic chemicals [40]. Organo-surfactants which are non-biodegradable have also been reported in raw municipal wastewater [34]. The removal of these chemicals is important before the effluent is discharged to the environment or water bodies. A thorough understanding of how these chemicals are distributed in the wastewater is necessary to design a good process for their removal.

Domestic sewage wastewater is categorized as either grey or black water. Though the bulk of domestic sewage COD is natural organic matter, the presence of foreign compounds like throwaway pharmaceutical compounds, washing chemicals, and other household chemicals make the effluent complex and variable from time to time. Some of the main natural matter composition of domestic wastewater COD was reported as fibre (20%), proteins (12%) and sugars (10%) [33]. These compounds were mainly found in supracolloidal range; an observation supported by a different study where sequential micro and ultrafiltration of domestic wastewater found that most of the COD was above 450 nm [3]. A separate PSD study on domestic wastewater observed the binomial distribution of particles [41].

In some processes, the separation of the grey and black fractions of domestic wastewater is done for effective treatment, especially where the reuse of treated grey water is anticipated. The separation ensures that the reuse water is less contaminated with microbes. It is thus important to analyse the composition of the two streams separately for effective treatment. An investigation of domestic wastewater by sequential filtration and laser diffraction observed a distinction between the particle size distribution in the black and grey fractions of the wastewater [29]. The COD in the black water was predominantly particulate while that in grey water was soluble [29]. It was also observed that in the soluble region, most proteins were in particle size region 14–220 nm [29]. The low COD and the presence of other compounds like washing surfactants and other chemicals in grey water makes biological treatment less effective when compared to black water. Membrane filtration is one of the final treatment methods for the grey fraction. The process is highly preferred where the treated effluent is meant for the reuse because it can remove the compounds that are resistant to biodigestion and physical-chemical treatments. It is possible to characterize the distribution of contaminants on basis of hydrophobicity. This is useful in membrane treatment processes whose performance is affected by the hydrophobicity of substrate particles. A study on the dissolved organic fractions of domestic waste treatment plant effluent observed that the hydrophobic compounds were the most dominant fraction with up to 70% composition [42]. The summary of the usage of PSD to characterize the COD fractions of municipal wastewaters is given in Table 2.

4. Characterization of effluents by analysing the biodegradability of the COD size fractions

The general understanding of the municipal effluent is that it is readily biodegradable. However, it is important to note that the biodegradability of this wastewater like most other wastewaters varies with COD size fractions of the influent. A detailed study of how the biodegradability varies with COD size fractions of biological wastewater would shed light on how the same happens in other substrates. Some of the compounds which affect the biodegradability of COD in many influents include the presence of toxicants, inhibitors or refractory substances. The distribution of these compounds is not uniform among the wastewater contaminants. This indicates that the biodegradability varies among the COD size fractions. It also implies that some COD fractions may be more responsible for the toxicity or non-biodegradability of the influent substrate than other fractions [41]. In such events, the prior knowledge of how the particles are distributed in the wastewater can help in the design of a process targeting those fractions for their removal or treatment. It is thus important to characterize the influent contaminants according to their biodegradability distribution. The COD can be classified according to biodegradability in the following categories; readily biodegradable soluble, slowly hydrolysable (Sh), soluble inert (Si) biodegradable particulate (Xs) and inert particulate (Xi) as shown in Figure 2.

Table 2. The COD particle size distribution in municipal wastewaters.

Wastewater type	COD (mg/l)	COD fractions	Abundance (%)	BOD fraction	Abundance (%)	Reference
Municipal wastewater	–	<0.001 µm	18–50	–	–	[25]
		0.001–1 µm	9–19			
		1–100 µm	10–31			
		>100 µm	15–43			
Sanitary landfill leachate WW	16,400	<0.002 µm	55	–	–	[43]
		0.002–0.0035 µm	3			
		0.0035–0.008 µm	5			
		>0.008 µm	37			
Domestic WW	440	<0.45 µm	26	–	–	[3]
		0.45–1.6 µm	9			
		>1.6 µm	65			
Settled sewage	513 (TS)	<0.001 µm	68	–	–	[1]
		0.001–1 µm	6			
		1–100 µm	11			
		>100 µm	15			
Secondary effluent	348 (TS)	<0.001 µm	90	–	–	[1]
		0.001–1 µm	8			
		1–100 µm	2			
Settled domestic WW	300	>1 µm	40	–	–	[44]
		0.45–1 µm	25			
		0.22–0.45 µm	3			
		<0.45 µm	49			
Municipal WW		–	–	S_i	5–10	[45]
				S_S	10–30	
				X_h	15–20	
				X_i	5–20	
				X_s	40–60	
Settled domestic WW	431	–	–	S_i	2	[46]
				S_S	10	
				X_i	7	
				$X_s + X_h$	80	
Sewage		–	–	S_s	23-32	[47]
				S_i	2.5-4	
				X_s	52-67	
Domestic black water	1010	–	–	Ss	14.6	[29]
				Sh	29.7	
				Si	3.6	
				Xs	50.7	
				Xi	1.3	
Domestic WW	–	–	–	Ss	23.5	[33]
				Si	20	
				Xs	41.5	
				Xi	3.5	
				Biomass	11.5	
Domestic grey water	370	–	–	Ss	29	[29]
				Si	5	
				Xs	65.5	
				Xi	1.5	

The heterotrophic biomass and associated microbial products form another category of the COD fractions for the wastewater from biological processes [48]. Other than activated sludge processes, there is limited documentation on the distribution of BOD fractions in other processes. The biodegradability of the wastewater is normally expressed through its BOD/COD ratio. High BOD/COD ratio (>0.5) implies good biodegradability while low values (<0.2) implies poor biodegradability. In the domestic sewage wastewater, the average ratio of five-days BOD to COD, (BOD_5/COD) for both the soluble and particulate COD fraction was found to be 0.47 [49]. However, only 14% of the COD was non-biodegradable while almost 80% was slowly biodegradable [49]. A separate study on the biodegradation of domestic sewage COD found that 23-32% was soluble biodegradable, 2–4% was soluble inert, 52–67% was particulate biodegradable and 7–15% was inert particulates [47]. In another study, the biodegradability of the settleable COD (13%) was slightly higher than that of the total COD (9%) in domestic sewage [50].

The fore knowledge of biodegradability distribution among COD substrate size fractions is particularly important where biological treatment aims at the recovery of energy through biodigestion. This helps in the choice of pretreatment method which increases biodegradability of some fractions without affecting those that are readily biodegradable. The treatment of municipal wastewater and associated sludge entails the use of

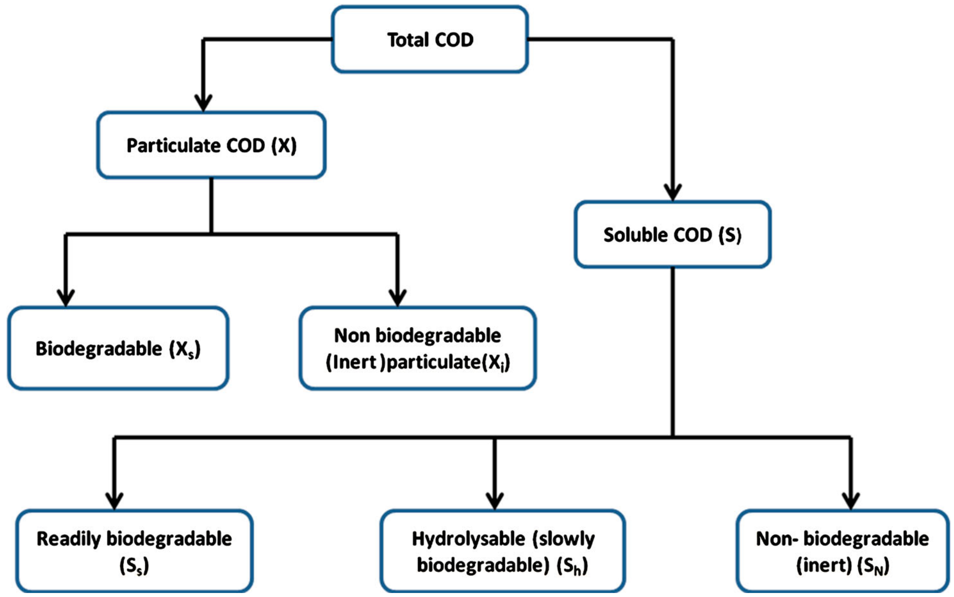

Figure 2. COD fractionation by biodegradability.

biological treatment for elimination of COD and energy recovery through biogas fermentation. The characterisation of biodegradability in the three COD fractions in municipal wastewater reported that the readily hydrolysable contents were up to 80% and 90% for the colloidal and soluble COD fractions respectively [51]. However, for the particulate fraction, most COD (45–50%) was slowly hydrolysable [51]. This implies that the residence time of the treatment process is mostly determined by the particulate fraction of the substrate.

5. Application of PSD in mapping out membrane foulants

The membrane filtrations and membrane bioreactors are among the most applied processes in the treatment of wastewater [52]. The fouling of membranes by wastewater contaminants is the biggest challenge to membrane treatment processes. It is possible to use PSD to map out the distribution of foulants in wastewater. The membrane fouling is contributed by several factors which include; feed substrate (e.g. its load, composition and COD-sludge ratio), foulants characteristics (e.g. their nature, size and distribution), process parameters (e.g. temperature, pH and ionic strength), process properties (e.g. flux, cross-flow velocity, space width and temperature) and membrane properties (e.g. pore size, hydrophobicity, surface functional groups, roughness and charge) [13]. According to the Darcy law, the total membrane resistance (R_t) is a sum of three resistances: the membrane resistance (R_m), the foulant resistance (R_f) and the cake resistance (R_c). The cake resistance is a function of particle size and is calculated as below:

$$R_C = \frac{(180C^2)}{d^2(1-C)_3}, \quad (1)$$

where C is the concentration of solids and d is the particle diameter. This implies that a thorough understanding of effluents contaminants distribution by PSD can help predict the membrane resistance.

There are different types of foulants in any biological wastewater and each will affect the process differently depending on the type of filtration. In ultrafiltration, colloids were found to be most responsible for membrane fouling [53]. Other researchers observed that biopolymer particles are most responsible for fouling in the ultrafiltration of biologically treated domestic wastewater [54]. The main mechanism through which fouling occurs is via the formation of a stagnant cake above the membrane by particulate matter especially the colloidal organics [55]. In addition to reducing the flux, the foulants can reduce the permeability of other particles by binding onto them or even block the membrane pore completely [56].

In most applications, the pretreatment of substrates influent before membrane treatment is necessary because it reduces fouling and increases the flux and membrane durability by preferentially removing the fouling fractions. A PSD study with six types of influents treated with different technologies found that aerobic digestion was better in removing high molecular weight particles than the anaerobic method [6]. It is possible to use chemicals like coagulants [57], and adsorbents [58] to selectively remove foulants before filtration processes. Another PSD study with domestic sewage treated biologically observed that the hydrophobic COD fraction which contributed most to flux reduction during the ultrafiltration was eliminated by adsorption and flocculation pretreatments [59].

In exceptional cases, the influent pretreatment has been observed to reduce permeate flux and increase fouling [13]. A PSD study of undigested MDW feed to filtration process found that the presence of big particles in the influent served as a dynamic cake which through abrasion effects helped clean the membrane thereby increasing the permeate flux [13]. The pretreatment using 0.45 μm paper filter resulted in decreased flux and high membrane fouling. The findings are supported by other reports which indicated that adsorbent particles could decrease rejection and increase the flux infiltration processes [60]. A thorough understanding of foulants distribution in the influent helps in the design of optimal pretreatment processes that help improve subsequent filtration processes. The prior knowledge of foulants PSD is also important during the choice of the membranes cut-off diameter. The cut-off determines the size of the particles to be eliminated during the filtration process. All the particles larger than the cut-off value are eliminated whereas most of those smaller pass-through subject to other factors like dynamic cake formation and membrane reactive properties.

Another use of PSD is in the analysis of microbial products (MP) which are produced in biological processes and are arguably the main source of membrane fouling. The production of microbial compounds in wastewater has been reviewed [61]. The microbial products may result from the modifications of organic substrates during biological treatment. Some of the products and secretions released by microbes during the process of biological treatment of wastewater include humics, organic acids, polysaccharides, fulvic substances, enzymes, proteins, antibiotics, steroids etc. Other studies have indicated that the extracellular polysaccharides which are microbial products are most responsible for the membrane fouling [62,63]. A study on polysaccharides produced in an MBR showed that the capsular polysaccharides and lipopolysaccharides products from gram-negative bacteria caused the highest membrane fouling [64]. It is also possible for the organic compounds in the feed to be transformed into other compounds which are associated with biomass and soluble microbial products (SMP). This may also result in the formation of both humic and hydrophobic compounds which contribute to membrane fouling [65]. A PSD study found that SMP contributed to 15% of total COD in a membrane bioreactor treating the sewage [66]. The formation of microbial products which cause membrane fouling is facilitated by certain process conditions. A good understanding of the causes and distribution of microbial products can help minimize their formation and thereby improve the influent treatment by membrane processes.

6. The PSD and mathematical models for effluents analysis

Another method of applying PSD in the treatment of wastewater is in the development of mathematical models for describing the changes in influent composition. In process engineering, relevant parameters are used to form a model equation which predicts the process behaviour or its performance. For example, a wastewater model would give a mathematical correlation between the number of particles and physical parameters like suspended solids, COD and turbidity. The use of model equations to describe COD particles of the influent and effluent of three wastewater treatment processes; submerged biofilter, rotating biological contactor and trickling filter has been reported [4]. By modelling the distribution of influent and effluent COD particles in the treatment process, it is possible to establish a correlation for determining the efficiency of the particle removal. The insight of how the knowledge of contaminant particles' distribution can help enhance the design of treatment processes was demonstrated using filtration and flocculation models [67].

The activated sludge models I, II and III (ASM 1 ASM 2 & ASM 3) by IWA apply the principle of particle size distribution to characterize the COD in primary and secondary effluents [68,69]. The model recognizes soluble COD (S) and particulate COD (X) as the two main COD classification. They also utilize the classification of COD in terms of its biodegradability and are based on the following COD categories: readily biodegradable soluble (Ss), volatile fermentation products (Sv), inert non-biodegradable soluble (Si), slowly biodegradable soluble (Xs), inert non-biodegradable particulate (Xi), heterotrophic biomass (XH), autotrophic biomass (Xaut) and phosphorus accumulating organisms (XPAO). The activated sludge models help to predict the increase and decrease of COD in the reactor.

Mathematical models have been used to describe the formation and degradation of microbial products in biological wastewater treatment [70,71]. They are based on existing models on the activated sludge thus based on PSD analysis. The microbial products can be categorized as biomass associated products, utilization associated products or extracellular polysaccharides. They can be soluble or insoluble with the latter contributing most to the membrane fouling. A model of membrane fouling based on mixed liquor of suspended solids, PSD of activated sludge and extracellular polysaccharide has been suggested [72].

7. Effect of wastewater treatment on the substrate's COD particle distribution

The knowledge of particle size distribution in the influent water and wastewater is necessary to design an integrated treatment process. Various wastewater treatment processes affect the particle size distribution and biodegradability characteristics of the substrates' COD particles differently. For example, some treatment processes will have preferential removal of certain COD fractions compared to other treatment methods [73]. In the primary settling step of MWWP, 35% of particulate COD was eliminated compared to 2% for the soluble and colloidal portions [73]. The subsequent biological digestion also had higher particulate COD removal compared to the other two fractions [73]. The difference in removal for the former is caused by the settling velocities of various fractions. The variation in the later is caused by hydrolysis of influent's particles to smaller ones through biodigestion. It is, therefore, necessary to have a clear understanding of how each treatment process affects individual COD fractions and the effect of this on subsequent treatment processes. The PSD of the activated sludge wastewater, which was bimodal in distribution, revealed a radical shift with most COD particles being found in the soluble region and few in the particulate region after the treatment with ozone [74].

There are a few documentations on how various wastewater treatment processes affect the COD particle fractions, their biodegradability characteristics and distribution in different influents. The changes on the particle characteristics caused by the treatment process will ultimately have some effects on the overall efficiency of the treatment process used. Most wastewater treatment processes will have preferential removal of certain COD fractions over others [75]. Ultrafiltration was found to remove almost 70% of hydrophobic fractions but less than 20% hydrophilic ones [75]. A review of how different COD fractions in wastewater can be removed by different treatment methods has been documented [76]. The particulate COD in domestic sewage was reported to have selective removal compared to the soluble fraction [1]. In addition to the contamination from the natural particles, the formation and breakdown of particles like flocs during the treatment process affect the parameters of the wastewater. In advanced primary treatment system of municipal wastewater, the sand filter flow rates higher than 10 m/h altered PSD of the flocs and caused their breakage which led to increase in suspended solids, colour, and turbidity [77]. Some treatment processes like advanced oxidation processes result in breakage of large particles and solubilization of organic matter which alters the substrate's PSD [78].

8. Discussion and future prospects of PSD technique

The municipal wastewaters are among the common complex effluents with varying particle composition. Their COD particle sizes range from soluble to huge particles [29,41,42]. In the primary effluent, both soluble and particulate fraction forms the bulk of COD. However, in secondary effluent, the bulk of COD is in soluble range due to sedimentation of the huge particles during the treatment. The biodegradability of the COD is dependent on the particle size. Most COD in domestic sewage is particulate and slowly hydrolysable [29,47].

The prior knowledge of PSD and biodegradability distribution for the influent COD can be useful in the choice of the method for treatment. For a slowly hydrolysable fraction of municipal effluent, an additional step of hydrolysis is necessary to break the complex substrate into smaller compounds to enable biodigestion. Small particles have a large surface area to volume ratio which implies that the particle breakdown of organic matter increases with the surface area on which microbes would attack. This implies that the pretreatment methods which are able to break the sludge into simpler compounds increase its biodegradability. The soluble COD is generally the most biodegradable fraction because of the presence of simple sugars and disaccharides. There are however some exceptions to this where big particles are most biodegradable as observed with the landfill leachate [79]. This is contributed by the presence of toxicants or inhibitors in the soluble fraction. It is possible to use the fraction analysis of the biodegradability to map out the toxicity distribution in the wastewater [80,81]. This is helpful in determining the pretreatment process of wastewater before discharge. If the recalcitrants or toxicity is on large particles, membrane separation can be used to eliminate them. However, if the same is concentrated on the small particles, processes like advanced oxidation processes can be used to increase its biodegradability for further treatment to enable safe disposal or reuse [82,83].

The knowledge of particle size distribution can be useful in the prevention of membrane fouling by enabling the engineer to understand the fraction of COD most responsible for it. The most influential resistance to the permeate flux in membrane filtration is the foulants resistance [84]. This resistance is largely dependent on the particle nature and size, process conditions and the properties of the membrane [85,86]. The pretreatment process targets and preferentially eliminates or modifies the foulants before actual filtration is done. The main membrane foulants in biological processes are the soluble microbial products (SMPs) which are integral components of anaerobic wastewater. They can be analysed by PSD methods. The SMPs contribute to the influent COD and the protein contents. There are documented reports on the usage of PSD in the analysis of SMP in complex organic wastewaters [5,87]. The formation of a dynamic membrane which is important in filtration processes is dependent on the substrate particle size distribution. The utilization of dynamic membranes in the treatment of wastewater has been reviewed [88]. Application of PSD in the analysis of foulant particles in the back-washing step of membrane filtration observed that backwashing step removed mainly large foulant particles [89]. The foulants in the influent can be selectively removed by various pretreatments like coagulation [90,91]. The COD particle distribution is important in the analysis of foulants in the influent after pretreatment which helps in determining the appropriate membrane for the treatment.

The idea of a mathematical model has been successfully applied to describe the processes in anaerobic digestion of municipal effluent. However, this should not only be limited to the activated sludge processes but can be modified for applications in other biological processes. The knowledge has been applied to make models that are applicable to membrane bioreactors. These models are based on the principle of COD fractionation by particle size and biodegradability. However, the investigations on the models for most bioreactors are still in laboratory scale [92]. In addition to analysing the distribution of COD particles, models can be used to investigate the distribution of flocs of different sizes during membrane separation. They can also be used to study the prevalence of target compounds like nutrients in the flocs [93]. Moreover, it has been shown that the activated sludge models can be modified for application in other processes like tannery industry wastewater [94] or in modelling of microbial products in bioreactors [95,96]. These models ought to be harmonized and simplified to contain fewer parameters for ease of adoption and application. The prior knowledge of mathematical models of individual processes like flocculation and sedimentation can help in the design of a good water treatment process. There are also reports documenting the usage of model equations in the determination of PSD for the rough membranes and for calculation of the interaction on the interfaces [97]. It is expected that more models for other processes will be developed in future based on the existing knowledge.

The wastewater treatment methods result in alteration of particle distribution in the reactor. The coagulation process removes some COD particles and helps in the flocs formation. The knowledge of PSD can be used to determine the selective removal of various COD fractions and the size distribution of the flocs formed by coagulation [98]. Adsorption process operates by surface binding of contaminants to the adsorbent. The ability of the particles to bind on the adsorbent is dependent on their charge and surface properties and can be selective on targeted pollutants [99]. This alters the distribution of particles in the substrates. A model on how adsorbent particles attach and detach from the surface can help in the design of the treatment process. The ability of advanced oxidation processes (AOPs) like ozonation to mineralize organic substrates to smaller particles makes them good pretreatment process to biodigestion. Ozonation was found to selectively mineralize the unsaturated compounds thus altering the particle distribution in the substrates [100]. In many applications, the influent treatment entails a combination of several unit operations [79]. A hybrid reactor combining coagulation and adsorbents in membrane filtration was found to improve the filtration process by removing the foulant fraction [101]. It is also possible to combine AOPs with other processes like biological and filtration processes [102]. The prior knowledge of the distribution of the target compounds in various COD fractions helps in the choice of integrated process for maximum foulants removal and for minimization of process costs.

Analysis of the effluent using PSD should not be limited to municipal effluents but can also be done on all wastewaters. Good understanding of the particle distribution would give good insight into the method of treatment and several studies on the same are documented. A PSD analysis of the olive mill wastewater (OMW) found that the polyphenols were concentrated in the low molecular weight fractions [103]. The PSD, in this case, is useful in determining the treatment process because the polyphenols inhibit biodigestion of OMW. Selective elimination of polyphenols by AOPs can be done to remove the inhibitors [104]. It is also possible to recover polyphenols for nutritional use because of their antioxidant activity [105–107]. In such applications, selective fractionation by membranes is normally applied [108,109]. The application of the PSD method on the pulp and paper wastewater indicated that most COD was less than 0.008 µm [8]. However, in polymer industrial wastewater, most COD was found to lie in the colloidal range [110]. A PSD study with raw molasses distillery wastewater found that most of the COD (>53%) was small particles and the coloured recalcitrants in the same had a particle size above 5 kDa, [13]. The high soluble fraction in MDW is due to particles like simple sugars and disaccharides which account for more than 50% total molasses solids [111]. These sugars are readily biodegradable hence eliminated in the digested effluent. However, the colourants which are mainly melanoidins and related compounds are recalcitrants [112]. Melanoidins are a high recalcitrants particles of size range (1–100 kDa) formed by the reaction of amino acids and sugars at alkaline conditions [112]. The use of PSD in the characterization of melanoidins would shed light on the most recalcitrant size fraction of melanoidins and the ideal conditions for their formation. Recent reports indicate that there is a high concentration of microplastics in water bodies which is a health hazard [113]. Most of these particles find their way into water through the release of treated effluent [114]. The analysis by PSD has been used to investigate the microplastic particle distribution in wastewater treatment plants from southern California [115]. The conventional treatment was found to be effective in removing plastic contaminants of micro size range [115]. It is expected that the analysis of emerging contaminants which are very hazardous shall make use of the application of PSD for greater accuracy.

The traditional methods of COD particle analysis were based on simple technologies like; sieving, centrifugation, gel filtrations, micro and ultrafiltration, and sedimentation. These methods had many limitations in their applications. The methods required a high quantity of sample for analysis to be carried out. The procedures of analysis were very cumbersome and time-consuming. Above all, the methods had poor resolution and were prune to huge errors. The recent advancements in analysis technology have transformed the COD particle analysis in many ways. As the environmental regulations concerning wastewater treatment become more stringent, the need to use advanced technologies for analysis of the influent and effluent of wastewater treatment processes will rise. The application of modern analysis technologies in the prediction of the distribution of various target pollutants will increase. The modern methods of analysis like laser diffraction and resonance mass measurements are not only fast but have simple set ups. The use of digital image analysis enables the real-time analysis of the samples. The sophisticated technologies like liquid chromatography organic carbon detection (LC-OCD) and high-performance size exclusion chromatography enable high-resolution analysis using very small COD sample. Other advanced analysis technologies which have found usage in the analysis of foulants in wastewaters include; Raman spectrometry[116], Fourier Transform Infrared [117], laser digital methods [118], Attenuated Total Reflectance, Fourier Transform Infrared (ATR-FTIR) spectrometry [119,120]. It is expected that with the rapidly advancing particle analysis technologies, the COD analysis in wastewater will undergo a great transformation. This will help in the design of good wastewater treatment methods and the control of the contaminants in the effluents. It is also expected that the new analysis technologies will have more applications in PSD analysis of wastewater contaminants.

9. Conclusion

The traditional methods of analysing the PSD of wastewater COD which include sieving and gel filtrations are limited in that they are cumbersome and slow. Upcoming technologies include methods like laser light scattering, Coulter counter, Malvern counter and LC-OCD which are fast and require a small sample. The usage of these new methods is on a rapid increase and is expected to cause a great impact on wastewater analysis. The treatment processes for wastewater affects the PSD of the treated effluent. In an integrated treatment process, it is important to understand how each treatment step alters the distribution of COD fractions in that unit operation and how this affects the subsequent treatment steps. It is possible to map out foulants in the treatment influent by using PSD analysis. The colloidal particles are the main foulants in the influent from biological processes. The PSD analysis of foulants can also be of great help in the design of a good process for the pretreatment and final membrane treatment of foulants. The analysis of wastewater contaminants by use of PSD can be applied in all types of wastewaters. It can be used to map out other parameters in the wastewater like distribution of heavy metals, phenolics, toxicants and colourants in various COD fractions.

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References

[1] Rickert DA, Hunter JV. General nature of soluble and particulate organics in sewage and secondary effluent. Water Res. 1971;5:421–436.

[2] Huber SA, Balz A, Abert M,W, et al. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography-organic carbon detection-organic nitrogen detection (LC-OCD-OND). Water Res. 2011;45:879–885.

[3] Dulekgurgen F, Doğruel S, Karahan Ö, et al. Size distribution of wastewater COD fractions as an index for biodegradability. Water Res. 2006;40:273–282.

[4] García-Mesa JJ, Poyatos JM, Delgado-Ramos F, et al. Water quality characterization in real biofilm wastewater treatment systems by particle size distribution. Bioresour Technol. 2010;101:8038–8045.

[5] Kunacheva C, Stuckey DC. Analytical methods for soluble microbial products (SMP) and extracellular polymers (ECP) in wastewater treatment systems: a review. Water Res. 2014;61:1–18.

[6] Barker DJ, Mannucchi GA, Salvi SM, et al. Characterisation of soluble residual chemical oxygen demand (COD) in anaerobic wastewater treatment effluents. Water Res. 1999;33:2499–2510.

[7] Bolong N, Ismail AF, Salim MR, et al. A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination. 2009;239(1-3):229–246.

[8] Leiviskä T, Nurmesniemi H, Pöykiö R, et al. Effect of biological wastewater treatment on the molecular weight

distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent. Water Res. 2008;42:3952–3960.
[9] Yaman FB, Çakmakcı M, Karadağ D, et al. Molecular weight distributions in cotton-dyeing textile wastewaters. Desalination Water Treat. 2016;57(27):12684–12691.
[10] Logan BE, Wagenseller GA. Molecular size distributions of dissolved organic matter in wastewater transformed by treatment in a full-scale trickling filter. Water Environ Res. 2000;72:277–281.
[11] Insel G, Dagdar M, Dogruel S, et al. Biodegradation characteristics and size fractionation of landfill leachate for integrated membrane treatment. J Hazard Mater. 2013;260:825–832.
[12] Chang YJ, Shih YH, Su CH, et al. Comparison of three analytical methods to measure the size of silver nanoparticles in real environmental water and wastewater samples. J Hazard Mater. 2017;322:95–104.
[13] Arimi MM, Namango SS, Götz G, et al. The abrasion effects of natural organic particles on membrane permeability and the size distribution of recalcitrants in a coloured effluent. J Membr Sci. 2016;509:1–9.
[14] Chang MR, Lee DJ, Lai JY. Nanoparticles in wastewater from a science-based industrial park-coagulation using polyaluminum chloride. J Environ Manag. 2007;85(4):1009–1014.
[15] Wassie AB, Srivastava VC. Teff straw characterization and utilization for chromium removal from wastewater: kinetics, isotherm and thermodynamic modelling. J Environ Chem Eng. 2016;4:1117–1125.
[16] Chaignon V, Lartiges B, El Samrani A, et al. Evolution of size distribution and transfer of mineral particles between flocs in activated sludges: an insight into floc exchange dynamics. Water Res. 2002;36:676–684.
[17] Chavez A, Jimenez B, Maya C. Particle size distribution as a useful tool for microbial detection. Water Sci Technol. 2004;50:179–186.
[18] Sanchis MIA, Saez J, Lloréns M, et al. Particle size distribution in slaughterhouse wastewater before and after coagulation-flocculation. Environ Prog. 2003;22:183–188.
[19] Marcato CE, Pinelli E, Pouech P, et al. Particle size and metal distributions in anaerobically digested pig slurry. Bioresour Technol. 2008;99:2340–2348.
[20] Ma H, Allen HF, Yin Y. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. Water Res. 2001;35:985–996.
[21] Marroquin M, Vu A, Bruce T, et al. Location and quantification of biological foulants in a wet membrane structure by cross-sectional confocal laser scanning microscopy. J Membr Sci. 2014;453:282–291.
[22] Sochan A, Polakowski C, Łagód G. Impact of optical indices on particle size distribution of activated sludge measured by laser diffraction method. Ecol Chem Eng S. 2014;21(1):137–145.
[23] Stetefeld J, McKenna SA, Patel TR. Dynamic light scattering: a practical guide and applications in biomedical sciences. Biophy Rev. 2016;8(4):409–427.
[24] Dogruel S, Olmez-Hanci T, Kartal Z, et al. Effect of Fenton's oxidation on the particle size distribution of organic carbon in olive mill wastewater. Water Res. 2009;43:3974–3983.
[25] Levine AD, Tchobanoglous G, Asano T. Size distributions of particulate contaminants in wastewater and their impact on treatability. Water Res. 1991;25:911–922.
[26] Masse L, Masse D, Beaudette V, et al. Size distribution and composition of particles in raw and anaerobically digested swine manure. Trans-Am Soc Agri Eng. 2005;48:1943–1949.
[27] Murugananthan M, Raju GB, Prabhakar S. Separation of pollutants from tannery effluents by electro flotation. Separ Purif Technol. 2004;40:69–75.
[28] Stoller M. On the effect of flocculation as pretreatment process and particle size distribution for membrane fouling reduction. Desalination. 2009;240:209–217.
[29] Hocaoglu SM, Orhon D. Particle size distribution analysis of chemical oxygen demand fractions with different biodegradation characteristics in black water and gray water, CLEAN-soil, Air. Water (Basel). 2013;41:1044–1051.
[30] Li Y, Lau SL, Kayhanian M, et al. Particle size distribution in highway runoff. J Environ Eng. 2005;131(9):1267–1276.
[31] Yu RF, Chen HW, Cheng WP, et al. Simultaneously monitoring the particle size distribution, morphology and suspended solids concentration in wastewater applying digital image analysis (DIA). Environ Monitor Assess. 2009;148:19–26.
[32] Zheng X, Ernst M, Jekel M. Identification and quantification of major organic foulants in treated domestic wastewater affecting filterability in dead-end ultrafiltration. Water Res. 2009;43:238–244.
[33] Huang M, Li Y, Gu G. Chemical composition of organic matters in domestic wastewater. Desalination. 2010;262:36–42.
[34] Dignac MF, Ginestet P, Rybacki D, et al. Fate of wastewater organic pollution during activated sludge treatment: nature of residual organic matter. Water Res. 2000;34:4185–4194.
[35] Sophonsiri C, Morgenroth E. Chemical composition associated with different particle size fractions in municipal, industrial, and agricultural wastewaters. Chemosphere. 2004;55:691–703.
[36] Bae TH, Tak TM. Interpretation of fouling characteristics of ultrafiltration membranes during the filtration of membrane bioreactor mixed liquor. J Membr Sci. 2005;264:151–160.
[37] Tiehm A, Herwig V, Neis U. Particle size analysis for improved sedimentation and filtration in waste water treatment. Water Sci Technol. 1999;39(8):99–106.
[38] Nakada N, Tanishima T, Shinohara H, et al. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Res. 2006;40(17):3297–3303.
[39] Lishman L, Smyth SA, Sarafin K, et al. Occurrence and reductions of pharmaceuticals and personal care

products and estrogens by municipal wastewater treatment plants in Ontario, Canada. Sci Tot Environ. 2006;367(2-3):544–558.
[40] Mitch WA, Sedlak DL. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. Environ Sci Technol. 2004;38 (5):1445–1454.
[41] Noyan K, Allı B, Tas DO, et al. Relationship between COD particle size distribution, COD fractionation and biodegradation characteristics in domestic sewage. J Chem Technol Biotechnol. 2017;92:2142–2149.
[42] Imai A, Fukushima T, Matsushige K, et al. Characterization of dissolved organic matter in effluents from wastewater treatment plants. Water Res. 2002;36:859–870.
[43] Campagna M, Çakmakcı M, Yaman FB, et al. Molecular weight distribution of a full-scale landfill leachate treatment by membrane bioreactor and nanofiltration membrane. Waste Manag. 2013;33:866–870.
[44] Hu Z, Chandran K, Smets BF, et al. Evaluation of a rapid physical–chemical method for the determination of extant soluble COD. Water Res. 2002;36(3):617–624.
[45] Henze M. Characterization of wastewater for modelling of activated sludge processes. Water Sci Technol. 1992;25(6):1–15.
[46] Orhon D, Sözen S, Ubayo E. Assessment of nitrification-denitrification potential of Istanbul domestic wastewaters. Water Sci Technol. 1994;30(6):21.
[47] Sadecka Z, Jedrezak A, Płuciennik-Koropczuk E, et al. COD fractions in sewage flowing into polish sewage treatment plants. Chem Biochem Eng Quart. 2013;27:185–195.
[48] Janus T, Ulanicki B. ASM1-based activated sludge model with biopolymer kinetics for integrated simulation of membrane bioreactors for wastewater treatment. Proc Eng. 2015;119:1318–1327.
[49] Orhon D, Ates E, Sözen SEU. Characterization and COD fractionation of domestic wastewaters. Environ Poll. 1997;95:191–204.
[50] Çokgör EU, Sözen S, Orhon D, et al. Respirometric analysis of activated sludge behaviour-I. Assessment of the readily biodegradable substrate. Water Res. 1998;32:461–475.
[51] Ginestet P, Maisonnier A, Sprandio M. Wastewater COD characterization: biodegradability of physico-chemical fractions. Water Sci Technol. 2002;45:89–97.
[52] Skouteris G, Hermosilla D, Lopez P, et al. Anaerobic membrane bioreactors for wastewater treatment: a review. Chem Eng J. 2012;198-199:138–148.
[53] Aehl R, Leiknes T, Ødegaard H. Tracking particle size distributions in a moving bed biofilm membrane reactor for treatment of municipal wastewater. Water Sci Technol. 2006;53:33–42.
[54] Zheng X, Ernst M, Huck PM, et al. Biopolymer fouling in dead-end ultrafiltration of treated domestic wastewater. Water Res. 2010;44:5212–5221.
[55] Guo W, Ngo HH, Li J. A mini-review on membrane fouling. Bioresour Technol. 2012;122:27–34.
[56] Lewis WJ, Mattsson T, Chew YJ, et al. Investigation of cake fouling and pore blocking phenomena using fluid dynamic gauging and critical flux models. J Membr Sci. 2017;533:38–47.
[57] Yu W, Xu L, Qu J, et al. Investigation of pre-coagulation and powder activate carbon adsorption on ultrafiltration membrane fouling. J Membr Sci. 2014;459:157–168.
[58] Zhang Q, Singh S, Stuckey DC. Fouling reduction using adsorbents/flocculants in a submerged anaerobic membrane bioreactor. Bioresour Technol. 2017;239:226–235.
[59] Shon HK, Vigneswaran S, Kim IS, et al. The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization. Water Res. 2004;38:1933–1939.
[60] Meier J. Mechanical influence of PAC particles on membrane processes. J Membr Sci. 2010;360(1-2):404–409.
[61] Barker DJ, Stuckey DC. A review of soluble microbial products (SMP) in wastewater treatment systems. Water Res. 1999;33:3063–3082.
[62] Le-Clech P, Chen V, Fane TAG. Fouling in membrane bioreactors used in wastewater treatment. J Membr Sci. 2006;284:17–53.
[63] Lin H, Zhang M, Wang F, et al. A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: characteristics, roles in membrane fouling and control strategies. J Membr Sci. 2014;460:110–125.
[64] Kimura K, Nishimura SI, Miyoshi R, et al. Application of glyco-blotting for identification of structures of polysaccharides causing membrane fouling in a pilot-scale membrane bioreactor treating municipal wastewater. Bioresour Technol. 2015;179:180–186.
[65] Jarusutthirak C, Amy G. Understanding soluble microbial products (SMP) as a component of effluent organic matter (EfOM). Water Res. 2007;41:2787–2793.
[66] Lu SG, Imai T, Ukita M, et al. Modeling prediction of membrane bioreactor process with the concept of soluble microbial product. Water Sci Technol. 2002;46(11-12):63–70.
[67] Lawler DF. Particle size distributions in treatment processes: theory and practice. Water Sci Technol. 1997;36:15–23.
[68] Henze M, Gujer W, Mino T, et al. Activated sludge models ASM1, ASM2, ASM2d and ASM3; 2000.
[69] Petersen B, Vanrolleghem PA, Gernaey K, et al. Evaluation of an ASM1 procedure on a municipal-industrial wastewater treatment plant. J Hydroinf. 2002;4:15–38.
[70] Zuthi MFR, Ngo H, Guo W, et al. A review towards finding a simplified approach for modelling the kinetics of the soluble microbial products (SMP) in an integrated mathematical model of membrane bioreactor (MBR). Int Biodeter Biodegrad. 2013;85:466–473.
[71] Jiang T, Myngheer S, De Pauw DJ, et al. Modelling the production and degradation of soluble microbial products (SMP) in membrane bioreactors (MBR). Water Res. 2008;42(20):4955–4964.
[72] Meng F, Zhang H, Yang F, et al. Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactors. Separ Purif Technol. 2006;51(1):95–103.

[73] Doğruel S. Biodegradation characteristics of high strength municipal wastewater supported by particle size distribution. Desalin Water Treat. 2012;45:11–20.
[74] Grady CL, Kirsch EJ, Koczwara MK, et al. Molecular weight distributions in activated sludge effluents. Water Res. 1984;18:239–246.
[75] Shon HK, Vigneswaran S, Kim IS, et al. Fouling of ultrafiltration membrane by effluent organic matter: a detailed characterization using different organic fractions in wastewater. J Membr Sci. 2006;278:232–238.
[76] Shon HK, Vigneswaran S, Snyder SA. Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. Crit rev Environ Sci Technol. 2006;36:327–374.
[77] LandaH CA, Jimenez B. Particle size distribution in an effluent from an advanced primary treatment and its removal during filtration. Water Sci Technol. 1997;36:159–165.
[78] Li X, Peng Y, He Y, et al. Applying low frequency ultrasound on different biological nitrogen activated sludge types: an analysis of particle size reduction, soluble chemical oxygen demand (SCOD) and ammonia release. Int Biodeter Biodegrad. 2016;112:42–50.
[79] Pi KW, Li Z, Wan DJ, et al. Pretreatment of municipal landfill leachate by a combined process. Process Saf Environ Prot. 2009;87:191–196.
[80] Gursoy-Haksevenler BH, Dogruel S, Arslan-Alaton I. Effect of ferric chloride coagulation, lime precipitation, electrocoagulation and the Fenton's reagent on the particle size distribution of olive mill wastewater. Int J Glob Warm. 2014;6:194–211.
[81] Klinkow N, Oleksy-Frenzel J, Jekel M. Toxicity-directed fractionation of organic compounds in tannery wastewater with regard to their molecular weight and polarity. Water Res. 1998;32(9):2583–2592.
[82] Arimi MM, Zhang Y, Namango SS, et al. The reuse of recalcitrant-rich anaerobically digested effluent as dilution water after biodegradability enhancement by Fenton processes. J Environ Manage. 2016;168:10–15.
[83] Bijan L, Mohseni M. Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents. Water Sci Technol. 2004;50(3):173–182.
[84] Chen J, Zhang M, Li F, et al. Membrane fouling in a membrane bioreactor: high filtration resistance of gel layer and its underlying mechanism. Water Res. 2016 Oct 1;102:82–89.
[85] Fane AG, Fell CJ. A review of fouling and fouling control in ultrafiltration. Desalination. 1987;62:117–136.
[86] Wang Z, Wu Z. A review of membrane fouling in MBRs: characteristics and role of sludge cake formed on membrane surfaces. Sep Sci Technol. 2009;44(15):3571–3596.
[87] Malamis S, Andreadakis A. Fractionation of proteins and carbohydrates of EPS in a MBR. Bioresour Technol. 2009;100:3350–3357.
[88] Li L, Xu G, Yu H. Dynamic membrane filtration: formation, filtration, cleaning, and applications. Chem Eng Technol. 2018;41(1):7–18.
[89] Akhondi E, Zamani F, Law AW, et al. Influence of backwashing on the pore size of hollow fiber ultrafiltration membranes. J Membr Sci. 2017;521:33–42.
[90] Ly QV, Nghiem LD, Cho J, et al. Insights into the roles of recently developed coagulants as pretreatment to remove effluent organic matter for membrane fouling mitigation. J Membr Sci. 2018;564:643–652.
[91] Huang BC, Guan YF, Chen W, et al. Membrane fouling characteristics and mitigation in a coagulation-assisted microfiltration process for municipal wastewater pretreatment. Water Res. 2017;123:216–223.
[92] Naessens W, Maere T, Nopens I. Critical review of membrane biorector models -part 1: biokinetic and filtration models. Bioresour Technol. 2012;122:95–106.
[93] Zhang B, Yamamoto K, Ohgaki S, et al. Floc size distribution and bacterial activities in membrane separation activated sludge processes for small-scale wastewater treatment/reclamation. Water Sci Technol. 1997;35:37–44.
[94] Karahan Ö, Dogruel S, Dulekgurgen E, et al. COD fractionation of tannery wastewaters-particle size distribution, biodegradability and modeling. Water Res. 2008;42:1083–1092.
[95] Ahn YT, Choi YK, Jeong HS, et al. Modeling of extracellular polymeric substances and soluble microbial products production in a submerged membrane bioreactor at various SRTs. Water Sci Technol. 2006;53(7):209–216.
[96] Aquino SF, Stuckey DC. Integrated model of the production of soluble microbial products (SMP) and extracellular polymeric substances (EPS) in anaerobic chemostats during transient conditions. Biochem Eng J. 2008;38(2):138–146.
[97] Zhao L, Zhang M, He Y, et al. A new method for modeling rough membrane surface and calculation of interfacial interactions. Bioresour Technol. 2016;200:451–457.
[98] Lee DG, Bonner JS, Garton LS, et al. Modeling coagulation kinetics incorporating fractal theories: comparison with observed data. Water Res. 2002;36(4):1056–1066.
[99] Dakiky M, Khamis M, Manassra A, et al. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. Advan Environ Res. 2002;6(4):533–540.
[100] Lee Y, von Gunten U. Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res. 2010;44(2):555–566.
[101] Kim J, Deng Q, Benjamin MM. Simultaneous removal of phosphorus and foulants in a hybrid coagulation/membrane filtration system. Water Res. 2008;42(8-9):2017–2024.
[102] Lin YH. Molecular weight distribution of organic matter by ozonation and biofiltration. Water Sci Technol. 2012;66:2604–2612.
[103] Dammak I, Neves M, Isoda H, et al. Recovery of polyphenols from olive mill wastewater using drowning-out crystallization based separation process. Innov Food Sci Emerg Technol. 2016;34:326–335.

[104] Afify AS, Mahmoud MA, Emara HA, et al. Phenolic compounds and COD removal from olive mill wastewater by chemical and biological procedures. Aust J Basic Appl Sci. 2009;3:1087–1095.
[105] Bertin L, Ferri F, Scoma A, et al. Recovery of high added value natural polyphenols from actual olive mill wastewater through solid phase extraction. Chem Eng J. 2011;171:1287–1293.
[106] Gursoy-Haksevenler BH, Arslan-Alaton I. Evidence of inert fractions in olive mill wastewater by size and structural fractionation before and after thermal acid cracking treatment. Separ Purif Technol. 2014;154:176–185.
[107] Arslan-Alaton I, Olmez - Hanci T, Dulekgurgen E, et al. Assessment of organic carbon removal by particle size distribution analysis. Environ Eng Sci. 2009;26:1239–1248.
[108] Castro-Muñoz R, Yáñez-Fernández J, Fíla V. Phenolic compounds recovered from agro-food by-products using membrane technologies: an overview. Food Chem. 2016;213:753–762.
[109] Russo C. A new membrane process for the selective fractionation and total recovery of polyphenols, water and organic substances from vegetation waters (VW). J Membr Sci. 2007;288(1-2):239–246.
[110] Doğruel S, Çokgör EU, Ince O, et al. Potential of ultrafiltration for organic matter removal in the polymer industry effluent based on particle size distribution analysis. Environ Sci Pollut Res. 2013;20:340–350.
[111] Arimi MM, Zhang Y, Götz G, et al. Antimicrobial colorants in molasses distillery wastewater and their removal technologies. Int Biodeter Biodegrad. 2014;87:34–43.
[112] Coca M, Garcıá MT, González G, et al. Study of coloured components formed in sugar beet processing. Food Chem. 2004;86(3):421–433.
[113] Murphy F, Ewins C, Carbonnier F, et al. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ Sci Technol. 2016;50(11):5800–5808.
[114] Talvitie J, Mikola A, Koistinen A, et al. Solutions to microplastic pollution-removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. Water Res. 2017;123:401–407.
[115] Carr S, Liu J, Tesoro AG. Transport and fate of microplastic particles in wastewater treatment plants. Water Res. 2016;91:174–182.
[116] Virtanen T, Reinikainen SP, Kögler M, et al. Real-time fouling monitoring with Raman spectroscopy. J Membr Sci. 2017;525:312–319.
[117] Benavente L, Coetsier C, Venault A, et al. FTIR mapping as a simple and powerful approach to study membrane coating and fouling. J Membr Sci. 2016;520:477–489.
[118] Yu Y, Yang Z, Duan Y. Structure and flow calculation of cake layer on microfiltration membranes. J Environ Sci. 2017;56:95–101.
[119] Howe KJ, Ishida KP, Clark MM. Use of ATR/FTIR spectrometry to study fouling of microfiltration membranes by natural waters. Desalination. 2002 Sep 10;147(1-3):251–255.
[120] Gong H, Jin Z, Wang Q, et al. Effects of adsorbent cake layer on membrane fouling during hybrid coagulation/adsorption microfiltration for sewage organic recovery. Chem Eng J. 2017;317:751–757.