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Abstract:

In response to the growing global resource scarcity, wastewater is increasingly seen as a valuable resource to recover and valorise for the benefit of the society rather than another waste that needs treatment before disposal. Conventional wastewater treatment plants (WWTPs) oxidises most of the organic matter present in wastewater, instead of recovering it as a feedstock for biomaterials or to produce energy in the form of biogas. In contrast, an A-Stage is capable of producing a concentrated stream of organic matter ready for valorisation, ideally suited to retrofit existing large plants. This technology is based on the principle of high-rate activated sludge process that favours biosorption and storage over oxidation. In this paper, we summarize peer-reviewed research of both pilot-scale and full-scale studies of A-Stage process under real conditions, highlighting key operational parameters. In the majority of published studies, the Sludge Retention Time (SRT) was identified as a key operational parameter. An optimal SRT of 0.3 days seems to maximize the redirection of influent COD – up to 50% to the sludge flux, while simultaneously keeping mineralization under 25% of total influent COD. Other key optimal parameters are a hydraulic residence time of 30 min and dissolved oxygen levels of 0.5 $mg \cdot L^{-1}$. In addition, nutrient removal efficiencies of 15-27% for total nitrogen and 13-38% for total phosphorus are observed. Influence of mixing on settling efficiencies remain largely underexplored, as well as impact of wet weather flow and temperature on overall recovery efficiencies, which hinders to provide recommendations on these aspects. Evolution of modelling efforts of A-Stage process are also critically reviewed. The role of extracellular polymeric substances remain unclear and measures differs greatly

according to the different studies and protocols. Better understanding the settling processes by adding Limit of Stokesian and Threshold of Flocculation measures to Sludge Volume Index could help to reach a better understanding of the A-Stage process. Reliable modelling can help new unit processes find their place in the whole treatment chain and help the transition from WWTPs towards Wastewater Resource Recovery Facilities.

List of Abbreviations

ASM	Activated Sludge Model	MLVSS	Mixed Liquor Volatile Suspended Solids
BMP	Biochemical Methane Potential	PHA	PolyHydroxyAlkanoates
BOD	Biochemical Oxygen Demand	PNA	Partial Nitritation-Anammox
CAS	Conventional Activated Sludge	PST	Primary Sedimentation Tanks
COD	Chemical Oxygen Demand	SRT	Solids Residence Time
CEPT	Chemically Enhanced Primary Treatment	SS	Suspended Solids
CSTR	Continuous Stirred Tank Reactor	SVI	Sludge Volume Index
DO	Dissolved Oxygen	TAG	TriAclyGlycerides
EPS	Extracellular Polymeric Substances	TOF	Threshold of Flocculation
F/M ratio	Food to Microorganism ratio	VFA	Volatile Fatty Acids
HRT	Hydraulic Residence Time	VSS	Volatile Suspended Solids
HRAS	High Rate Activated Sludge	WAS	Waste Activated Sludge
LOSS	Limit of Stokesian settling	WWRF	Water Resource Recovery Facility
MLSS	Mixed Liquor Suspended Solids	WWTP	Wastewater Treatment Plant

1. Introduction

“Doing more with less” is the new paradigm of the International Water Association in order to fulfil the Sustainable Development Goal 6 “Clean Water and Sanitation” by 2030 (IWA, 2016). For municipal wastewater treatment, this paradigm requires a transition from Wastewater Treatment Plants (WWTPs) to Water Resource Recovery Facilities (WRRFs). There is a growing societal need expressed by stakeholders such as companies operating WWTPs and local water authorities, who are looking for sustainable solutions for treatment requirements. Organic matter present in raw wastewater is a source of chemical energy and

can hence be considered as a resource. Approximately 6.9 kJ of free energy is contained in 1 L for wastewater with an average concentration of 500 mg $COD \cdot L^{-1}$ (McCarty et al., 2011). Traditionally, primary sedimentation tanks (PSTs) redirect some of the influent organics to produce primary sludge, which is then anaerobically digested to generate biogas to offset the energy needs of the WWTP. However, PSTs have high space requirements and are quite inefficient in recovering this resource without chemical addition. Recovering organic matter prior to its oxidation is doubly advantageous as it minimizes aeration (energy) demand and simultaneously increases the methane produced (Wan et al., 2016). Among the best available process technologies that maximises recovery potential is a process based on high rate activated sludge (HRAS), also called A-Stage, which is the focus of this review. Main advantage of A-Stage over other technologies for recovery such as Chemically Enhanced Primary Treatment (CEPT) is relatively lower operational costs as usually no reagent is utilised (Wan et al., 2016).

The A-Stage is part of the A/B (Adsorption-Belebung) process that has originally been developed in the 1970s and 1980s in the Technical University of Aachen (Böhnke, 1977) to maintain nitrification process stability. The A/B process is a two-stage process consisting of two activated sludge processes in series, each with its own reactor, clarifier and independent sludge recirculation loops as shown in Figure 1. Essentially, a PST is replaced by the A-Stage process and can hence be considered a “biologically-enhanced” primary treatment. At the time of its development, the B-Stage was operated only for ammonia removal as a low-rate activated sludge process.

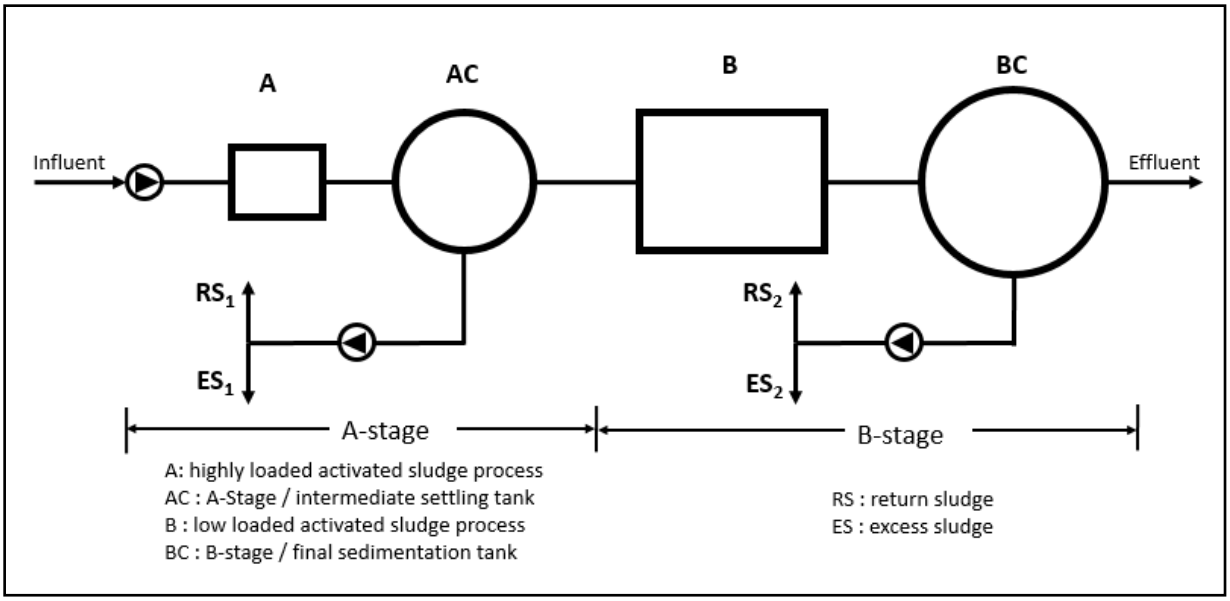

Figure 1 Simplified flow diagram of A/B process (Versprille et al., 1984)

A-Stage is characterised by its high organic loading rate (F/M ratio) coupled with low sludge age and short hydraulic residence times. There is no universally accepted definition of operating parameters of A-Stage; however, most authors use a limit solid residence time (SRT) of two days. A comparison of some key process parameters between the A-Stage and conventional processes is presented in Table 1.

Table 1 : Key operating parameters of A-Stage and other processes

	Process variant	SRT (days)	HRT (hours)	F/M ratio ($kgBOD \cdot kgMLVSS^{-1} \cdot day^{-1}$)
(Versprille et al., 1984)	A-Stage	< 2	0.5-1	3 – 6
	B-Stage	15-20	2-4	0.15 to 0.30
(Von Sperling, 2015)	CAS	4 to 10	6-8	0.25 to 0.50
	Extended aeration	18 to 30	16-24	0.07 to 0.15

The A/B process did not establish itself as a widely used process configuration because full mineralisation of nitrogen became an additional treatment requirement in the beginning of the 1990s. The increased carbon removal in the A-Stage hinders heterotrophic denitrification in

the B-Stage due to lack of sufficient organic carbon, and most A/B plants have been converted to conventional activated sludge (CAS) processes. Compared to CAS, the extended aeration process variant applies very long sludge ages in order to achieve high organic matter removal and aerobic stabilisation of the sludge.

However, two driving forces inspire the renewed interest in the A/B process in recent years. Firstly, the development in autotrophic N removal in the last two decades led to new approaches in coupling A-Stage and autotrophic N removal strategies such as Partial Nitritation / Anammox (PNA) (Dai et al., 2018; Gu et al., 2020, 2018). Secondly, the impacts of climate change (Mata et al., 2021) incites all sectors of human activity to minimize its contribution to the greenhouse effect. Developing waste valorisation technologies that can offset fossil fuel use has clear environmental benefits (Modin et al., 2016).

Recent reviews from Sancho et al. (2019) and Guven et al. (2019) compiled the relevant technologies for recovering influent organic carbon, focussing on a comparison of the main available carbon redirection technologies, highlighting the importance of A-Stage process. The review proposed by Rahman et al. (2020) gives an interesting evaluation of A-Stage and high rate contact stabilisation processes for carbon capture and highlights the interest of such processes to remove a significant amount of N and P in waste activated sludge (WAS). However, a detailed analysis of peer-reviewed studies on A-Stage studies, discussing its mechanisms as well as its challenges and drawbacks is lacking. This study aims to fill this gap, and additionally summarises the experience of full-scale implementations as well as attempts to model and simulate this process. Specific combinations of keywords were chosen for a search on webofknowledge.com and sciencedirect.com for studies on HRAS or A-Stage processes, the results of which are succinctly summarized in Table S1 (supplementary material). The search was continuously updated; the most recent update was performed end of December, 2021. Only original research articles were included. In addition, to be considered, the experimental conditions of the studies had to be clearly described, e.g. the size of the treatment units, duration and analytical procedures. The keyword search yielded in a total of

116 publications. The titles of studies were then screened according to their relevance to the topic, and, in case of a positive outcome, the abstract and full text were consulted. Additional screening was conducted to select only papers related to the scope of our investigations.

Thirty-eight publications dealt with HRAS or A-Stage processes. Two studies had to be excluded from further evaluation since crucial information was lacking (e.g. size of the experimental setups). In the end, 36 publications met the defined criteria, of which nine described investigations of “classical” A-Stage setups. The remaining articles were either HRAS-variants (such as High Rate Contact Stabilization (HiCS) and High Rate Sequencing Batch Reactors (HRSBR)), investigations conducted under static conditions, focusing on specific parameters (e.g. EPS) or in very small pilot scale (A-Stage reactor volume smaller than 1L), or review articles without any experimental data.

2. A-Stage Process: Current knowledge

During the initial development of A/B process technology, no particular attention was given to A-Stage technology and the focus was mainly on nitrogen removal in B-Stage as maintaining nitrification process stability was seen as a prime advantage (Versprille et al., 1984). As this technology is being revisited in view of its ability to redirect influent COD to a sludge stream, a better understanding of the mechanisms will be useful in design and operation. The current knowledge on the A-Stage process, starting with the driving mechanisms are summarized in the following sections. Then a section presenting results from laboratory-scale and demonstration-scale experiments is proposed including major influencing factors on carbon and nutrient capture. Finally, a section presenting most of the A-Stage or HRAS full-scale experiments published will be proposed before the discussion with the aim of highlighting the main challenges associated to the implementation of A/B process into WRRFs.

2.1. Mechanisms of Organic Matter Capture/Interactions

Organic matter present in the influent wastewater interacts with the return sludge in the A-Stage reactor in many complex mechanisms. Return sludge contains activated sludge flocs,

which are loosely bound amorphous structures that contain microorganisms embedded in a matrix of extracellular polymeric substances (EPS) (Ni and Yu, 2012). The major mechanisms of interaction are assimilation, biosorption and settling, which are conceptually represented in *Figure 2*. These mechanisms are a function of the properties of influent organic matter fractions, as well as the nature of the flocs of the return sludge.

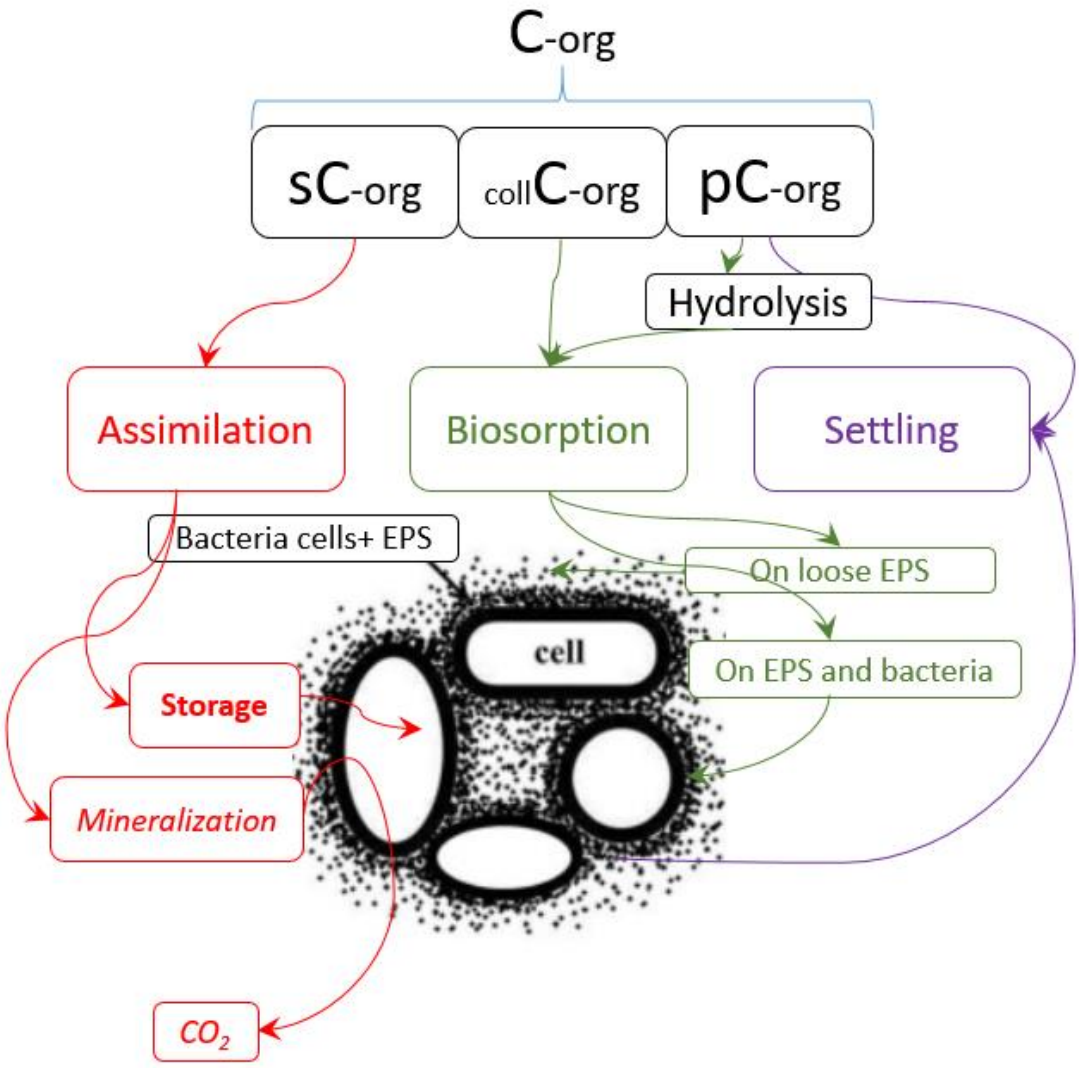

Figure 2 Schematization of interactions between bacteria and different fractions of organic carbon (C-org) (inspired by Modin et al., 2016)

Assimilation is a biological mechanism that removes part of the soluble, biodegradable fraction (biodegradable sC_{-org}) of the organic carbon molecules that are small enough to pass through the cell membrane. This fraction of biodegradable organic carbon serves both as

carbon source and electron donor for the microorganisms for cell growth, storage of polymers, or production of Extracellular Polymeric Substances (EPS), and for cell maintenance. Hence, a fraction of biodegradable sC_{-org} is oxidised to carbon dioxide and water by aerobic heterotrophic microorganisms. The ratio of microbial growth rate and oxidation rate is called yield (Y) (Von Sperling, 2015).

Microorganisms can store soluble biodegradable organic compounds in the form of intracellular inclusions. The soluble compounds after penetrating the cell walls are converted to insoluble polymers (such as polyhydroxyalkanoates (PHA), triacylglycerides (TAG), wax esters, etc.) to avoid build-up of high osmotic pressure across the cell membrane. Volatile Fatty Acids (VFAs) such as acetate will result in storage of PHAs whereas carbohydrates such as glucose will result in storage of glycogen. The bacteria are capable of reutilising the stored carbon for cell functions when no external carbon source is available, i.e., during a famine phase. Dynamic process configurations such as Sequencing Batch Reactors (SBRs) in which the activated sludge is exposed to periods of feast and famine, induce storage behaviour (Coats et al., 2011).

Biosorption is a combination of physico-chemical interactions that bind colloidal and particulate fraction ($collC_{-org}$ and pC_{-org}; biodegradable or not) of organic matter to activated sludge flocs by weak adhesive forces. There is no universally accepted definition of biosorption and various other terms are used to refer to this phenomenon such as sorption, enmeshment, bioflocculation, agglomeration, extra-cellular adsorption, etc. EPS may assist with this agglomeration, depending on its quantity, composition and surface properties (Kinyua et al., 2017a). In the sense of this article, biosorption describes an extra-cellular phenomenon, distinguished from storage, which is an intra-cellular phenomenon. Biosorption has been recognized as the key mechanism contributing to carbon capture and driving the interest in A-Stage systems.

Finally, settling is a physical phenomenon where agglomerates form in the A-Stage reactor and sufficiently large organic matter (pC_{-org}) settle to the bottom of the separation unit, typically

a surface clarifier. The settled sludge is either removed from the system, or recirculated back to the reactor.

2.2. Overall A-Stage performances: pilot- and demonstration-scale investigations

From the identified papers, nine articles at pilot and demonstration scale performed with real wastewater were selected. Information on experimental conditions of the reactor and influent-effluent characteristics are summarized in Table 2. There is a diversity in the scale of studies from laboratory scale to demonstration scale, but most common HRT was set to 30 min and SRT varied from 0.3 days to up to 2 days. Dissolved oxygen (DO) level in the reactor was set to 0.5 mg L^{-1} in all studies except two, where DO set point was of 2 mg·L^{-1}. Information on the influent and effluent COD was compiled when available. All considered studies used raw wastewater with total COD ranging from a low 300 mg·L^{-1} to more than 600 mg·L^{-1}. Likewise, information on fractions was compiled with colloidal fractions being measured following the protocol of Mamais et al. (1993) when available. This protocol of COD fractionation yields three fractions of COD, namely particulate COD (pCOD), colloidal COD (cCOD) and flocculated-filtered COD (ffCOD). Some studies followed an older and simpler fractionation that involves direct filtration at 0.45 µm resulting in only two fractions – particulate COD and filtered COD (fCOD). It can be seen that all studies achieved a tCOD removal of > 50%, with one study reaching up to 90% (Taboada-Santos et al., 2020), which can be considered an outlier. Examining the COD fractions of the effluent, most COD removal is due to the removal of pCOD, followed by ffCOD and lastly cCOD.

Table 2: Pilot and demonstration scale investigations: operating conditions and removal efficiencies

Reference	Reactor vol. (L)	Study period (d)	SRT (d)	HRT (h)	DO conc. ($mg \cdot L^{-1}$)	MLSS ($g \cdot L^{-1}$)	Inflow COD* ($mg \cdot L^{-1}$)	Removal efficiency (%)	Inflow nutrients ($mg \cdot L^{-1}$)	Nutrients Removal efficiency (%)
(Taboada-Santos et al., 2020)	2	65	1	2	3-3.5	2-3	t: 375-750 s: 80-150 p: 295-600	87 N/A N/A	 NH_4-N: 45 PO_4-P: 2.3	 19 13
(Diamantis et al., 2014)	3	36	0.3-0.5	0.9	2.0	2.1	t: 238 s: 80 p: 155	52 25 66	TKN: 55 NH_4-N: 33 PO_4-P: 3.8	12 13 10
(Koumaki et al., 2021)	15	14	0.25	0.6	>2	2.3	t: 675	68		
(Jimenez et al., 2015)	260	365	0.1-2	0.1-1	0.0-2.0	2.6	t: 480 ff: 110 c: 80 p: 290	75 90 55 75		
(Rahman et al., 2019)	510	N/A	0.3	0.5	0.5	3.7	t: 619 ff: 157 c: 67 p: 395	68 62 25 77	TKN: 45 NH_4-N: 35 TP: 6.1 PO_4-P: 4	18 19 35 46
(Kinyua et al., 2017a, 2017b)	510	63	0.3-0.6	0.5-1	0.5-1.5	2.6-3.5	t: 575 ff: 149 c: 85 p: 345	70 25 37 75		

(Wett et al., 2020) Singapore Pilot plant	1 000	N/A	N/A	0.5-0.75	N/A	N/A	t: N/A ff: N/A c: N/A p: N/A	82 13 30 94	TN: N/A TP: N/A	22 24
(Guven et al., 2020, 2017)	4 000	180	0.35	1-2.1	0.3-0.4	2	t: 486 s:242 p: 242	59 45 66	TN: 56 NH_4-N: 43 TP: 4.2	21 15 27
(Cao et al., 2020)	550 000	N/A	0.5	0.5	< 0.3	N/A	t: 660 ff: 132 c: 238 p: 290	64 48 21 100		

*t: total COD, s: filtered COD, ff: flocculated-filtered COD, c: colloidal COD, p: particulate COD

2.2.1. Influence of SRT on COD mass balance

COD mass balance is visually represented in Figure 3. It shows three possible transformations of influent COD upon leaving the A-Stage system.

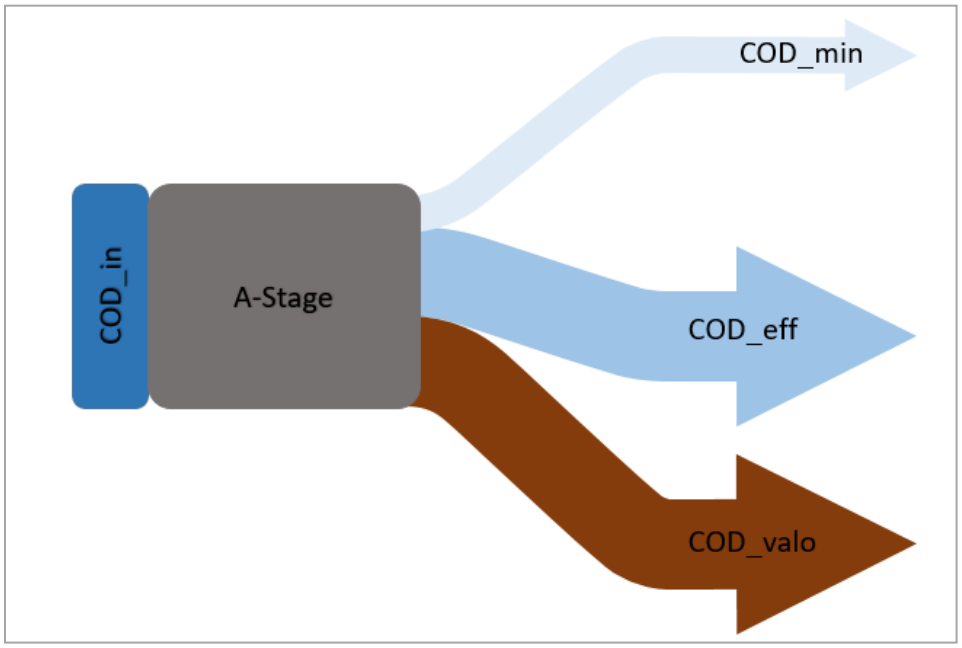

Figure 3 Visualisation of COD mass balance

It can be calculated based on daily performance data of the process in steady conditions from the following equation (considering no accumulation in the reactor):

$$\mathbf{COD\_in} = \mathbf{COD\_eff} + \mathbf{COD\_min} + \mathbf{COD\_valo} \quad (1)$$

Where:

- COD_in is the COD of influent;
- COD_eff is the COD of the A-Stage effluent;
- COD_min is the portion of COD that is lost as CO_2;
- COD_valo is the COD embedded in the waste sludge.

An optimized A-Stage process maximizes the portion of COD_in that is diverted to the sludge matrix (COD_valo), while simultaneously minimizing the mineralized fraction (COD_min), which is lost as CO_2 to the atmosphere. *Table 3* presents the mineralization rate reported in literature on A-Stage. The ratio of COD_valo to COD_in is the measure of the efficiency of the A-Stage process, which is referred to as carbon recovery efficiency (Cao et al., 2020) or carbon harvesting efficiency (Rahman et al., 2016). COD_eff is the fraction of

influent COD that leaves A-Stage to the next unit treatment process. Typically, COD_min is calculated using this equation, i.e., to close the mass balance, whereas the rest of the parameters are measured.

All studies that reported mineralization rates are presented in Table 3. Jimenez et al. (2015) concluded that the operational parameter with the highest influence on mineralization is the SRT, as longer SRT resulted in more mineralisation of COD. However, even under comparable SRTs, there is a substantial variation across different studies of the influent COD lost to the atmosphere as CO_2. These variations are possibly due to varying composition of influent COD, MLSS concentration, temperature in the reactor and other uncontrolled process operational parameters (Kinyua et al., 2017a). Influent COD fractions can play a major role on carbon redirection. If we consider that 1) the particulate COD fraction is mostly removed by primary settling linked to the efficiency of the settling system in the A-Stage process, 2) the soluble fraction is mostly linked to the bacterial assimilation and growth, and 3) the colloidal matter fraction is removed by biosorption on bacterial material and EPS, therefore the carbon redirection of an influent rich in particulate COD will be limited by the settling capacity, a effluent rich in colloidal COD will be limited by EPS production and collision probability with biomass and an effluent rich in soluble COD by the bacterial growing conditions.

Table 3 Reported mineralization and recovered sludge (as % of influent COD) in pilot- and demonstration-scale investigations

SRT (days)	0.1	0.3	0.5	1.0	2.0
	Mineralization / recovered sludge (as % of influent COD)				
(Jimenez et al., 2015)	14 / 31	N/A / 48	37 / 42	N/A / 29	67 / 23
(Kinyua et al., 2017a)		23 / 46	22 / 56		
(Cao et al., 2020)			24 / 41		
(Rahman et al., 2019)		23 / 43			
(Guven et al., 2017)		23 / 38			

Table 3 presents also the recovery rate of the sludge reported in the original research studies on classical A-Stage. Jimenez et al. (2015) reported a trend of decreasing recovery as SRT increased from 0.3 days to 2 days, which is in contradiction with the study of Kinyua et al. (2017a), much like for the opposing trends between the two studies observed for mineralisation rates. In the majority of published studies, SRT of 0.3 days seems to be the optimal SRT to maximise the capture of influent COD as sludge, even though it is largely variable and most likely dependant on other operational parameters and nature of organic matter present in influent wastewater. The optimal recovery value reaches 50% of the influent COD. By considering the different pathway of COD in A-Stage, several studies concluded that there is a threshold with an SRT ranking between 0.2 and 0.4 enabling to maximize carbon capture (Jimenez et al., 2015; Rahman et al., 2020).

2.2.2. Influence of DO and HRT on COD mass balance

DO has a key role in bacterial metabolism and settling efficiency. With regard to carbon mineralisation, several studies have shown that a balance has to be found between low DO level (< 0.5 $mg \cdot L^{-1}$) where bacterial growth, EPS production and settling efficiency are limited and high DO conditions (>1.5-2 $mg \cdot L^{-1}$) where mineralisation level and energy consumption are too high (Kinyua et al., 2017a, b; Jimenez et al., 2015).

Far fewer studies reported the impact of HRT on the COD recovery potential of A-Stage processes. Jimenez et al. (2015) investigating HRTs from 10 min to 60 min, concluded that a HRT of 30 min as optimal beyond which negligible increase in tCOD and sCOD removal were observed. A similar conclusion was reached by De Graaff et al. (2016) carrying out aerated jar tests on A-Stage sludge from full-scale plants. The authors observed that 15 min contact time (including the return stream) is sufficient for most sCOD removal. Guven et al. (2017) measured the impact of HRTs of 130, 95 and 60 min and found that the shortest HRT resulted in highest tCOD recovery in the sludge and lowest effluent TSS. The effect of HRT on COD recovery is considerable: if too short (less than 30 min) the contact time between the biomass and the substrate reduce the production of EPS and the overall COD removal decreases, if is

too long (generally larger than 1-1.5 hour), the carbon capture is not maximized and mineralisation becomes too high.

2.2.3. Nutrients removal in A-Stage

Capturing nutrients represents another benefit of an A-Stage process and is mostly linked to assimilation during bacterial growth combined with capture into WAS. Average removal rate ranking from 15-27% TN and 13-38% TP have been reported (Rahman et al., 2020). This could represent an interesting energy reduction in the downstream nutrient removal system. The SRT was observed to be a major factor influencing N removal with an increase of TN removal going from 22% at 0.5 d up to 49% at a 3 d (Ge et al., 2017). The same pattern was observed for TP removal going from ~15% at SRT< 1d up to 34 % at a 3 d SRT (Ge et al., 2017). Increasing the SRT improves the yield and therefore assimilation of nutrients but at the same time increases the mineralisation of COD (> 60% at a 3 d SRT). Therefore, the overall mass balance has to be considered to target the treatment strategy by either favouring carbon capture or nutrients removal. Typically, full-scale plants add metal salts in A-stage to achieve additional TP removal (see Section 2.3).

2.2.4. Role of EPS

EPS are microbial secretions and products of cellular lysis or hydrolysis. They are negatively charged and make up 50-80% of organic fraction in activated sludge. Proteins (PN) and polysaccharides (PS or carbohydrates) are its main constituents, making up 78-80% of EPS with the rest being other organic fractions such as humics, nucleic acids, lipids, etc., (Dignac et al., 1998). The EPS concentration present in the sludge is naturally a function of various operating parameters including SRT and DO levels as well as influent characteristics (Faust et al., 2014). .

It is hypothesized that both quantity and nature of EPS can play an important role in biosorption of colloidal and particulate matter into the activated sludge floc matrix in A-Stage systems. Table 4 presents the quantity of total EPS reported in different A-Stage systems as

a function of SRT at comparable DO levels. Two studies (Jimenez et al., 2015; Rahman et al., 2016) used the cation exchange resin (Frølund et al., 1996) method for EPS extraction. Whereas the rest of the studies, which are more recent, used the heat extraction method (Li and Yang, 2007). As of yet, no standard method or protocol for EPS measurement in activated sludge exists, making it challenging to compare and interpret the results meaningfully.

Table 4 : EPS measured in A-Stage sludge, varying SRT and DO conditions (Total EPS mg COD·g VSS^{-1})

		SRT (days)				
	DO (mg·L^{-1})	**0.16**	**0.3**	**0.5**	**1.5**	**2.0**
(Jimenez et al., 2015)[a,1]	*1.0*		50	105		125
(Rahman et al., 2016)[a,2]	*1.0*	230		308		367
(Van Winckel et al., 2019)[a,1]	*N/A.*				90	
(Kinyua et al., 2017)[b,1]	*1.0*		227	200		
(Rahman et al., 2019)[b,1]	*0.5*	165	123			

a: Cation Exchange Resin method; b: Heat extraction method; 1: Raw wastewater as influent; 2: CEPT effluent; N/A: not available

Table 4 presents EPS measured in the mixed liquor in A-Stage. In addition to the large heterogeneity in the total EPS found across the studies, its trend with respect to varying SRTs is also different depending on studies. Jimenez et al. (2015) observed increasing EPS concentrations with increasing SRTs, which concurs with Rahman et al. (2016). However, Kinyua et al. (2017a) and Rahman et al. (2019) observed the opposite trend studying two SRTs of 0.28 and 0.56 days, as well as 0.16 and 0.3 days respectively. Apparent differences in the reported values may be linked to measurement protocols as well as influent characteristics, MLSS concentrations, F/M ratio and other uncontrolled parameters. With regards to the capture of pCOD and cCOD, Jimenez et al. (2015) reported increasing EPS concentration increased their capture, whereas Kinyua et al. (2017a) found no correlation. More research is therefore needed to establish the part played by EPS – its total quantity and its nature, in aiding

organic matter capture through biosorption. EPS production is believed to improve carbon capture through colloidal COD capture mostly, although contradictory results have been published. Maybe the following hypothesis can be formulated: Tightly Bound (TB) fraction to the biological material can favour colloidal matter biosorption and settling, whereas Loosely Bound (LB) fraction EPS in suspension are more difficult to settle and can decrease the overall COD removal efficiency.

2.2.5. Settling characteristics

Settling is most commonly characterized by a measurement of Sludge Volume Index (SVI) following APHA (2005) which considers settling over 30 minutes. Table 5 presents the SVI reported in various A-Stage studies. Most studies report good (SVI < 150 mL· g TSS^{-1}) settling of A-Stage sludge with SVI values between 30-80 mL· g TSS^{-1} even across varying SRTs from 0.3 days to 1.5 days. Comparing SVIs across a large range of SRTs, Ngo and Massoudieh, (2021) show a sharp peak SVI of around 550 mg/L for an SRT of approx.. 3 days, with SVIs below 100 mg/L for SRTs below 2 days. However, a low SVI alone is not a sufficient criterion to judge the clarifier performance in an A-Stage: the TSS concentrations of the supernatant can still be unusually high, as observed by Guven et al. (2020) who reported an SVI < 50 mL· g TSS^{-1}, but effluent TSS concentrations higher than 150 mg·L^{-1}. This represents particulate and colloidal COD that could have been redirected to the waste sludge, but is instead “lost” in the effluent. This might be a consequence of the characteristics of the A-Stage mixed liquor where very small flocs are formed and sometimes not settling leading to high TSS concentration in the supernatant, the settled sludge could be made of particulate COD mostly.

Table 5 Settling properties of A-Stage sludge SVI30 [mL · g TSS^{-1}]

		SRT (days)		
Reference	**Study conditions**	**0.3**	**0.6**	**1.5**
(Guven et al., 2017)	HRT = 130 min	29		
	HRT = 60 min	18		
(Kinyua et al., 2017a)	DO = 0.5 mg·L^{-1}	76	155	
	DO = 1.5 mg·L^{-1}	72	109	
(Rahman et al., 2019)		88		
(Van Winckel et al., 2019)				88
(Wett et al., 2020)			50 – 80	

Studying the impact of HRT, Guven et al. (2017) concluded that in addition to improving the % COD recovered as sludge, the SVI also improved from HRT of 60 min compared to that of 130 min. Similarly, Rahman et al. (2019), Van Winckel et al.(2019) and Wett et al. (2020) all reported SVI between 50 and 90 mL·g TSS^{-1}, which is lower than that of conventional activated sludge, where SVIs lower than 150 mL/g is considered a fair value (Von Sperling, 2015). This contrasts with the findings of the review of (Sancho et al. 2019), where poor settling of A-Stage sludge is mentioned as the drawback that prevented a wider adaptation of A/B processes worldwide. In Kinyua et al. (2017a), overall lower SVI values at shorter SRT (0.3 days) could be due to the washout of filamentous organisms, the impact of DO was pronounced at higher SRT, presumably due to differences in types of filamentous organisms.

Research on conventional activated sludge indicated links between the composition of EPS of the sludge and its settling characteristics (Li and Yang, 2007). This method further characterizes EPS as Loosely Bound (LB) fraction and Tightly Bound (TB) fraction by stepwise extraction. The fractions are then analysed for their COD, protein content (PN) and polysaccharide content (PS). Two studies (Kinyua et al., 2017a; Van Winckel et al., 2019)

adopting this method for EPS extraction and characterization, explored a relation between settling and various A-Stage systems but did not find a conclusive relation between settling performance and EPS – neither total quantity nor its quality (such as PN/PS ratio). This could be intrinsically linked to the role of EPS in the capture of colloidal and particulate matter in the A-Stage reactor, as discussed in 2.2.4.

New metrics to characterize settling such as Limit of Stokesian settling (LOSS) (Mancell-Egala et al., 2016) and Threshold of Flocculation (TOF) (Mancell-Egala et al., 2017) were developed to overcome the limits of established solids flux theory. LOSS is the solids concentration of the sludge at which flocculent settling (Stokesian) transitions into hindered (non-Stokesian) settling, while TOF is the concentration limit to induce floc formation and consequently transition from discrete to flocculent settling. TOF is hence a measure of particle collision efficiency. It is hypothesized that if the mixed-liquor solids concentration is between LOSS and TOF, the clarifier performance is optimized with minimal TS loss in the effluent. Developing on this approach, very recent research (Ngo et al., 2021; Ngo and Massoudieh, 2021) proposes a relation between TOF and effluent suspended solids (via flocculent settling coefficient – r_p) and a second relation between EPS and TOF. This marks a first attempt in describing a relation between EPS content and effluent suspended solids, albeit indirectly. As these parameters and approaches were only recently introduced, little information is available in literature to validate the hypotheses.

In conclusion, it is challenging to predict the settling properties and effluent quality of A-Stage and certainly more research is needed to explore the links between quantity and properties of EPS and settling characteristics. Apart from TOF, LOSS and EPS measurement, other investigations could be performed to evaluate sludge settleability, including microscopic ones, measure of floc resistance to shear stress and measure of zeta potential of the flocs. To our knowledge, these investigations have never been applied to A-Stage mixed liquor.

2.2.6. Valorisation potential of A-Stage sludge

The most common valorisation pathway of the produced sludge is via anaerobic digestion to produce biogas, which is mainly a mixture of CH_4 and CO_2. The produced energy can offset the plant's own energy requirement or it can be sold. Biochemical Methane Potential (BMP) is a measure of cumulative methane produced as the organic matter in the sample degrades under anaerobic conditions. It is crucial in getting an insight into design parameters for anaerobic digesters (Holliger et al., 2016).

Table 6 presents the BMP from various A-Stage studies expressed as produced volume of methane under normal conditions of temperature and pressure, normalized to the amount of volatile solids introduced (NmL CH_4·g VS^{-1}). Choo-kun (2015) compared the BMP of sludge from primary settling, A-Stage, and a long sludge age process and found that A-Stage sludge had the higher BMP of 335 NmL CH_4/g VS, compared to 290 NmL CH_4 g VS^{-1} and 220 NmL CH_4 g VS^{-1} for primary sludge and secondary sludge from extended aeration, respectively. Hence, the BMP of A-Stage sludge is not so different from primary sludge. Other studies have reported BMP values in the same range, but comparison between studies is difficult as the influent wastewater characteristics – both quantity and quality of organic matter – can vary widely. The wide range reported by Trzcinski et al. (2016) shows the influence of intraday variations and high oil and grease content in the influent. Few energy recovery indices were proposed, such as Methane Recovery Index and Energy Recovery Index (Rey-Martínez et al., 2021). These indices are useful in comparing the overall recovery potential of different A-stage systems, however not enough information is available to calculate these indices for studies summarized in Table 6.

Table 6 Bio-Methane Potential of A-Stage sludge

Reference	BMP [NmL $CH_4.g^{-1}$ VS]	*Comments*
(Cao et al., 2020)	**359**	Demonstration scale study (274 $m^3 \cdot h^{-1}$) with 0.5 day SRT, DO < 0.3 $mg \cdot L^{-1}$ and 30 min HRT; 500 mL bottles used for BMP.
(Choo-kun, 2015)	**335**	Pilot scale (2 $m^3 \cdot h^{-1}$) with DO = 0.5 $mg \cdot L^{-1}$ and 30 min HRT. 5 L reactor used for BMP.
(Taboada-Santos et al., 2020)	**295**	Lab scale study (0.5 $L \cdot h^{-1}$) with DO = 3-3.5 $mg \cdot L^{-1}$ and 2 h HRT; 2 L reactor used for BMP.
(Trzcinski et al., 2016)	**460**	Pilot scale (42 $m^3 \cdot h^{-1}$) with SRT 0.5 day, DO = 0.3 $mg \cdot L^{-1}$ and 30 min HRT; 500 mL bottles used for BMP.

Another emerging valorisation pathway of the concentrated organics stream is the production of high value biopolymers such as Polyhydroxyalkanoates (PHA) that can be used to produce bioplastics. However, regulatory barriers and public acceptance of such products are of concern. Further research is required to make biopolymer production from waste sludge economically viable compared to plastics produced from fossil fuels (Gherghel et al., 2019).

2.3. Full-Scale Performance

In the 1970s and 1980s, A/B process has been successfully implemented in full-scale plants in some European countries especially in the Netherlands, Germany and Austria. As mentioned in introduction, the emergence of more stringent effluent requirements on nitrogen led to a decline in A/B systems, with some of them being reconfigured to CAS due to lack of organic carbon for achieving the required denitrification. The information that was found on existing full-scale A-Stage/HRAS implementation is summarized in Table 7.

Table 7 Summary of full-scale A-Stage installations and carbon capture full-scale plants

Location	Year Operational	Design max Capacity (P.E)	Details on A-Stage	Reference
Nieuwveer, NL	1992	440 000	3 500 m^3 plug flow tank	(De Graaff et al., 2016)
Dokhaven, NL	1988	564 000	4 800 m^3 plug flow tank	
Utrecht, NL	1976	480 000	3 750 m^3 CSTR**, square	
Garmerwolde, NL	2006	375 000	2 760 m^3 CSTR round	
Strass, AT	1999	200 000	644 m^3 CSTR	(Wett et al., 2020)
Vienna, AT	2020	4 000 000	N/A*	(Kroiss and Klager, 2018)
Blue Plains, Washington D.C., US	1969	8 700 000#	N/A	(Rahman et al., 2016)

* N/A = not available

** CSTR = Continuous-flow Stirred Tank Reactor

calculated based on 0.2 L per P.E

It can be noted that A-Stage has been implemented in large to very large treatment plants. In the case of the Nieuwveer plant which was originally built in 1976 and refurbished to A/B process in 1992, its original primary settlers were used as A-Stage settlers. The Vienna WWTP was undergoing an upgrade (at the time of publication of Kroiss and Klager 2018), however the existing PSTs were retained in the process scheme, and A-Stage treats PST effluent. The Vienna strategy is not a conventional A/B process as defined in our review but presents an interesting strategy by using a two-stage activated sludge with an HRAS receiving nitrates. Likewise, the Blue Plains plant also utilises A-Stage (HRAS) technology after a primary treatment step, in this case a CEPT process. All full-scale plants dose metal salts for phosphorus precipitation in the aeration tank, but concentrations used are not provided for any of them in the available literature. Without the concentrations of metal salts used, it is difficult to evaluate the effect of metal salt addition on COD valorisation efficiency and on settling. Wett

et al. (2020) observed no improvement in COD removal or settling performance up to a molar ratio of metal/P of 0.5.

Most of the publications presenting full-scale investigations focus on A-Stage and carbon removal strategy, few elements are provided on the B-Stage. The strategy presented at the Vienna plant rely on a full nitrification/denitrification process and an optimisation of carbon capture enabling enough redirection to perform full denitrification. Few options are available and rely on either full nitrification (in case no restriction are applied) or PNA processes. Recent reviews have shown that PNA processes are not completely mature for mainstream application; to our knowledge, no full-scale success stories have been reported. Challenges remains at several levels including implementing an intelligent control of partial nitrification, exploring the molecular biological mechanism of NOB selective inhibition and strengthening of pre-treatment process for partial nitrification (Wang et al., 2021).

Energy consumption data on A-Stage is not available for most plants, but it was reported as 0.17 and 0.10 kWh· kg $COD_{removed}^{-1}$ for Dokhaven and Utrecht, respectively (De Graaff et al., 2016). It is higher than the 0.08 kWh· kg $COD_{removed}^{-1}$ (calculated) reported by Wett et al., (2020). Little knowledge is available on the dynamic performance of the A-Stage process and how the drop in performance during rain events, or even sludge washout can be mitigated, which is a major drawback of A-Stage processes (Diamantis et al., 2014).

3. Discussion

3.1. Knowledge synthetized in models

Numerical models are made for representing reality in a more or less simplified way and are very useful when comparing different treatment configurations. In addition, they embed the current knowledge associated to a specific process. As far as short residence time processes such as A-Stage are concerned, modifications to ‘historical’ activated sludge models (ASM) were required. Widely used models like ASM1 are not suitable for systems with short residence times (< 2 days) as first recognized by Haider et al. (2003), since the biodegradable fractions

of organic matter was modelled as a single substrate and by a single removal kinetic (one Monod term), which is a valid assumption for sludge ages longer than 5 days. Moreover, these early models do not explicitly account for neither EPS production nor biosorption mechanisms, which play a key role in A-Stage process. These physico-chemical mechanisms were indeed not considered in the original ASMs, as they were not limiting for the considered sludge ages (>3 days in ASM1).

To model high-rate processes without increasing the complexity of the model, Smitshuijzen et al. (2016) modified ASM1 by introducing a factor ($f_{settler}$) that accounts for the fraction of biodegradable particulate matter that is captured by the A-Stage system. This factor accounts for both the efficiency of biosorption and the efficiency of separation in the settler in one term. It was estimated from data from the full-scale plant Dokhaven (Rotterdam, The Netherlands) including daily and seasonal variations to investigate the impact of rain events and changes in water temperature. The results show that the model was able to predict effluent total COD with a 10% error under steady-state conditions. The model was also able to describe the drop in COD removal in A-Stage during winter months (temperatures of 10-12°C) via dynamic simulations, which according to Smitshuijzen et al. (2016) is due to the decrease in heterotrophic activity at low temperatures rather than decrease in the efficiency of biosorption. Examining the data from another full-scale A-Stage plant, Wett et al. (2020) found the same relation of decreasing COD removal efficiency with decreasing temperatures. Contrarily, they argue that it cannot be explained by the Arrhenius effect on microbial growth and instead is rather by temperature sensitivity of biosorption reactions. It is clear that more research effort is needed to fully understand this relation. It can be however hypothesized that the decrease of temperature might reduce the frequency of collision between the colloidal matter and the floc / Tightly Bound EPS thus reducing biosorption. Lastly, it was reported that the Dokhaven plant uses iron salts for P-removal in A-Stage reactor (De Graaff et al., 2016), which was not mentioned in the context of the model development.

This simplified yet effective A-Stage model of Smitshuijzen et al. (2016) was further integrated into whole-plant modelling by Jia et al. (2020) in order to study the benefits and drawbacks of a coupled A-Stage-PNA (Partial Nitritation Anammox) system compared to a CAS system. The simulation results showed a trade-off between maximising COD capture for energy recovery and minimizing residual COD entering the autotrophic PNA reactor with operating conditions being an SRT of 0.3 to 0.5 days and DO of 0.3 to 0.5 mg/L. The study also found the A-Stage/PNA configuration led to an increase of 50% of COD recovery as sludge compared to a CAS plant, and 60% lower overall aeration energy, all the while meeting the EU discharge limits (EU Urban wastewater directive 91/271/EEC of 21 May 1991). In A-Stage/PNA configuration, the COD recovery is mostly linked to the A-Stage sludge, contribution of B-Stage sludge has been estimated as to a maximum of 10-12 % of COD redirection (Wan et al., 2016)

Nogaj et al. (2015) developed a more mechanistic approach to model high-rate processes by introducing additional state variables to ASM1 model. On a single biomass population two substrates were considered – fast and slow biodegradable organic matter with fast biodegradable fraction being considered as VFA concentration in the influent. Influent COD was split into three subparts with colloidal COD being considered explicitly as an additional state variable, which is an upgrade compared to ASM1. EPS was also added as a state variable, along with storage products and sorption of colloidal substrate. Hauduc et al. (2019) built upon this model by adding a new fast growing biomass and a further fractionation of fast biodegradable organic matter into VFAs and other organic compounds. Flocculation of colloidal particles is a rate limiting process in A-Stage systems and thus was modelled explicitly as a function of EPS present in the biomass. Furthermore, as flocculation is sensitive to temperature and mixing intensities, an empirical factor (range 0–1) on flocculation rate was introduced to account for deflocculation processes. Finally, storage products are modelled to reflect lower mineralization rates observed in A-Stage, and it is supported by experimental observations by Kinyua et al. (2017b). This study measured PHA production yields at different

SRTs (0.28 day and 0.56 day) and DO concentrations (0.5, 1.0 and 1.5 $mg \cdot L^{-1}$) without a dynamic feast-famine configuration. A maximum PHA concentration of 42 mg $COD \cdot gVSS^{-1}$ was found in the aerobic reactors at SRT of 0.28 days and DO of 1.0 $mg \cdot L^{-1}$ with a corresponding PHA yield of 1.20 g PHA COD $gVFA^{-1}$. PHA concentration were always higher at the lower SRT in this study. Literature on storage product formation in A-Stage is scare and more research is perhaps needed to further understand the contribution of storage and its influence on other operating parameters.

The new plant-wide model has the advantage of being valid in other biological process units with different operating conditions, without employing interface equations. It predicted low mineralization rates found in A-Stage systems. Colloidal concentrations in the effluent were also predicted thanks to explicit modelling of flocculation as a function of EPS content: the greater the quantity of EPS, the higher is the portion of captured colloids to form particulates. However, the bio-kinetic model can be quite sensitive to influent characterization, as it demands many fractions that are generally not measured – such as VFA and biomass concentration.

Moreover, in all the models, settling is still considered as an empirical process whereas due to the weakness of A-Stage flocs, floc disturbance at the inlet structure of A-Stage clarifier might have a big impact on its efficiency (Solon et al., 2019). Recent research by Ngo et al. (2021) attempts at predicting effluent concentrations by means of an empirical function using experimentally determined TOF value. They further developed this approach to link EPS characteristics and TOF (Ngo and Massoudieh, 2021). As EPS had already been included in the model as a function of operating parameters, the authors were able to predict effluent solids concentrations as a function of process conditions. Since this approach is very recent, there are no comparable studies in literature. Overall, more effort is needed to gain a clearer insight into floc formation processes, their dependence on temperature and mixing intensity within A-Stage systems and finally settling phenomena of A-Stage sludge. Implementing a strategy to improve floc densification in A-Stage could represent an interesting research topic such as

hydrocyclone-based wasting to achieve SVI improvements (Regmi et al., 2022) and/or use of bio-sourced polymeric substances.

3.2. Design recommendations

Based on the present review, optimal ranges for operating parameters of an A-Stage system are presented in Table 8. The parameters suggested may need to be adjusted based on the influent conditions, reactor configurations and other site-specific conditions, but provide a starting point based on consensus values in the available literature.

Table 8 Suggested operating and design parameters based on this review

Parameter	Suggested value based on this review
HRT	30 min
SRT	0.3 - 0.5 days
DO	0.5 $mg \cdot L^{-1}$
MLSS	2-3 $g \cdot L^{-1}$
Recirculation rate	0.5 - 1
Waste strategy / Sludge extraction	Target MLSS based control

Optimal operating parameters ultimately depend on the objective of A-Stage, which is most often to maximise COD_valo, but depending on the downstream processes, it could have an additional constraint on COD/N ratios of A-Stage effluent (Miller et al., 2016). To maintain the DO at 0.5 mg/L, most often aeration is provided by compressed air through diffusers at the bottom of the reactor. The ratio of oxygen transfer efficiency under process conditions compared to fresh water is referred to as α-factor, which is an important design parameter. Based on long-term studies, α-factor of A-Stage was determined to be 0.45 (Schwarz et al., 2021) under dry weather flow, which is similar to the factor suggested by Kroiss and Klager (2018) or for non-nitrifying CAS systems (Gillot and Héduit, 2008). Typical reported α-factor

CAS is in the range 0.60 to 0.75 for nitrifying systems, higher α-factor of 0.8 was found for B-Stage (Schwarz et al., 2021), which is attributed to the removal of surfactants and other inhibitors in the A-Stage. In high-loaded systems such as A-Stage reactors, constituents that hamper oxygen transfer – surfactants in particular - are indeed less degraded than in CAS, thus reducing oxygen transfer efficiency (Gillot and Heduit, 2008; Bencsik et al., 2022).

A sludge extraction control based on maintaining a constant MLSS concentration in the reactor was found to be optimal to buffer diurnal variations in influent COD concentrations (Miller et al., 2017). In the matter of separation unit design or sizing, little to no information is available in the literature. The clarifier to reactor volume ratio varies widely from 0.5 to 7 in the studies reviewed (see Table S2 supplementary material).

4. Conclusions and need for further research

The growing interest in recovering resources in municipal wastewater led to a resurgence in the interest in the A-Stage process technology, owing to its capacity to recover influent organic carbon and ease of integration into existing WWTPs. Recent research summarized in this review recognised EPS production and biosorption, including intracellular storage, as the dominant bio-chemical mechanisms involved in this technology. Key operational parameters that drive the process efficiency were also pointed out, as well as the observed limitations:

- To maximise the redirection of influent COD to the sludge flux, SRT was found to be the key parameter with an optimal value of 0.3 days. HRT and DO levels are also important operational parameters, with target values of 30 min and 0.5 $mg \cdot L^{-1}$, respectively.
- Optimal performances show a redirection of up to 50% of the influent COD to the sludge flux, while the mineralization can be kept below 25% of the influent COD.
- Published full-scale applications show a great variability in the observed performance that cannot be explained through the current knowledge on bio-chemical mechanisms.

Being a short retention time biological process, A-Stage is quite sensitive to fluctuating concentrations of COD in the influent. Especially in the case of a municipal plant receiving influent from a combined or a semi-separative sewer system, rain-induced dilution can destabilize the process that leads to a drop in performance and can even lead to sludge washout.

Challenges remain over the wide spread adoption of A-Stage technology despite its natural advantage over other similar processes such as CEPT that require expensive chemicals to operate. The following have been principally identified:

- A better understanding of A-stage performances requires further research on the operating parameters affecting them; especially temperature and mixing that are overlooked in the literature.
- Continuing the effort to better understand liquid-solid separation efficiency is also mandatory, starting with a better description of separation units in A-stage related publications. The relationship between biosorption and settling phenomena should be further investigated in a holistic manner.
- Conceptualisation of biosorption mechanism in numerical models can help accelerate research in this domain. This necessitates the characterization of new state variables and a finer influent fractionation.
- Observed impact on influent dilution calls for mitigation or avoidance strategies that might be useful to define the operating range of the system and especially to handle wet weather flows.

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