SINGLE SLUDGE ACTIVATED SLUDGE BIOLOGICAL TREATMENT OF CARBON, NITROGEN, AND PHOSPHORUS IN COMBINED MUNICIPAL AND INDUSTRIAL WASTEWATERS FROM THE KOHTLA-JÄRVE REGION OF ESTONIA

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The application of a single sludge activated sludge system to the treatment of combined municipal and industrial wastewaters from the Kohtla-Järve region of Estonia is evaluated as an option to meet the carbon, nitrogen, and phosphorus effluent requirements for discharge to the Baltic Sea as stipulated by the "Helcom Recommendations." Literature are reviewed and current facility operations data are developed to assess the potential of achieving nitrification, denitrification, and biological excess phosphorus removal with a wastewater treatment plant that processes industrial wastewaters that contain phenolics and other inhibitory organic compounds which can suppress ammonia-nitrogen oxidation by activated sludge. The evaluation concludes that single sludge activated sludge systems for biological nutrient removal may not be appropriate for the treatment of complex industrial wastewaters, and selection of this biological treatment process without first conducting pilot-scale tests to verify the performance of the technology in this application is not recommended.

Introduction

The wastewater treatment plant (WWTP) at the Kiviter Oil Shale Chemicals facility in Kohtla-Järve, Estonia, is a two-stage biological treatment system (Fig. 1). It treats industrial wastewater and sewage not only from Kiviter but also from other nearby industries and municipalities. This treatment plant presently treats between 28,000 and 36,000 m³/d of industrial and municipal wastewaters. The addition of several new industrial and municipal wastewater sources will increase the volume of wastewater for treatment to 55,000 m³/d.

First Stage   Second Stage

Aerobic   Aerobic

Return Activated Sludge

Existing Kohtla–Järve Biological Treatment Process

Return Activated Sludge

Nitrate Recycle

Anaerobic   Anoxic   Aerobic   Anoxic   Aerobic

Five–Stage Biological Nutrient Removal System (modified Bardenpho)

Return Activated Sludge

Nitrate Recycle

Anaerobic   Anoxic

Anoxic   Aerobic

Mixed Liquor
Recycle

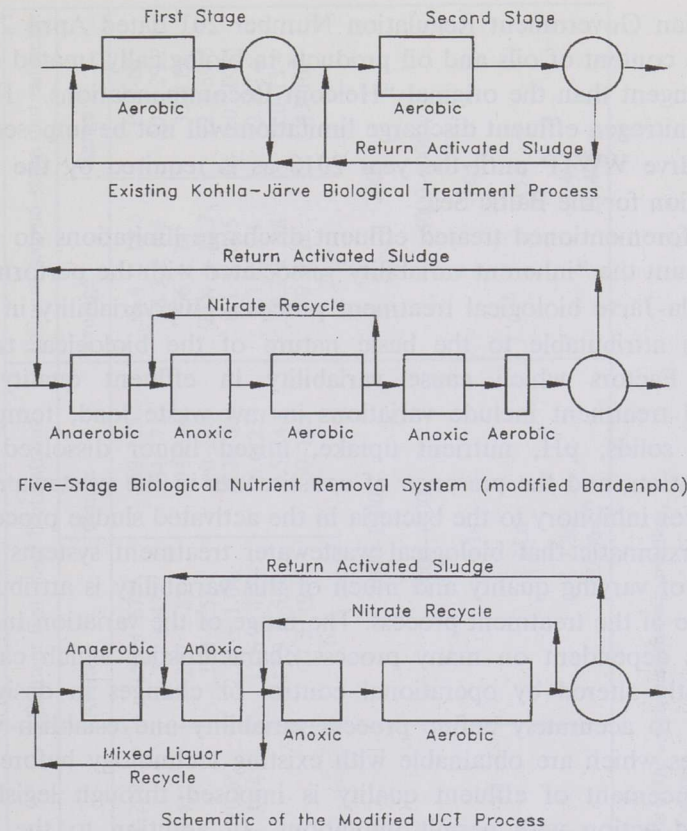Schematic of the Modified UCT Process

Fig. 1. Schematic layout for biological nutrient removal systems

At issue is the regional WWTP's ability in the future to meet the treated effluent requirements of the Helsinki Commission for the Baltic Sea as stipulated by the "Helcom Recommendations."

The Estonian Government has made the treated effluent quality requirements for wastewater discharges to surface waters and the sea more stringent than that originally proposed by the "Helcom Recommendations." These new requirements resulted from Estonian Government Regulation Number 464 dated December 15, 1994. This regulation requires that larger wastewater treatment facilities discharging to surface waters and to the sea are to meet the following treated effluent requirements:

Suspended solids	15 mg/L
Seven day biochemical oxygen demand	15 mg/L
Phenolics (volatile phenols)	0.1 mg/L
Total phosphorus	1.5 mg/L
Total nitrogen	10 mg/L
Oil products and shale oil	1 mg/L

Estonian Government Regulation Number 201 dated April 25, 1995, made the content of oils and oil products in biologically treated effluents more stringent than the original "Helcom Recommendations." However, the total nitrogen effluent discharge limitation will not be imposed on the Kohtla-Järve WWTP until the year 2010 as is required by the Helsinki Commission for the Baltic Sea.

The aforementioned treated effluent discharge limitations do not take into account the "inherent variability" associated with the performance of the Kohtla-Järve biological treatment process. This variability in effluent quality is attributable to the basic nature of the biological treatment process. Factors which cause variability in effluent quality during biological treatment include variations in raw waste load, temperature, dissolved solids, pH, nutrient uptake, mixed liquor dissolved oxygen concentration, and the presence of constituents in the wastewater which are toxic or inhibitory to the bacteria in the activated sludge process [1].

It is axiomatic that biological wastewater treatment systems produce effluents of varying quality and much of this variability is attributable to the nature of the treatment process. The range of the variation in effluent quality is dependent on many process characteristics which cannot be significantly altered by operational control or changes in design. It is necessary to accurately define process variability and establish variation allowances which are obtainable with existing technology before control and enforcement of effluent quality is imposed through legislative or ministerial action with permit limitations. In addition to the issue of effluent quality variability, there is the question of whether the treated effluent discharge limitations are achievable with conventional technology.

Existing Wastewater Treatment System

The municipal component of the regional wastewaters are pretreated in a section of the Kohtla-Järve WWTP which provides comminuting devices, vortex grit removal systems, and primary solids sedimentation. The industrial wastewaters, which include waste streams from the Kiviter dephenolization plant, Kiviter tar recovery plant, RA Eesti Kiviõli shale oil operations, Nitrofert production operations, Velsicol Eesti AS operations, and Püssi particle board manufacturing, are combined with the pretreated municipal wastewaters before entering aerated equalization basins in the main body of the WWTP. (The municipal wastewaters also include a portion of industrial wastewaters from those production factories that are connected to the municipal sewerage system - e.g., RAS Püssi-PPK.)

Table 1. **Influence of Treatment Stage on Kohtla-Järve WWTP Process Performance**

Parameter	Influent wastewater		Effluent first-stage biotreatment		Effluent second-stage biotreatment	
	Average	Range	Average	Range	Average	Range
Total*1 BOD_7, mg/L	205 ± 52	114-292	155 ± 57*2	69-255	39.4 ± 13.3	19.2-62
Settled*3 BOD_7, mg/L	—	—	82 ± 43	34-173	18.3 ± 6.6	10.1-29.2
Total BOD_{21}, mg/L	265 ± 78	176-411	207 ± 87	93-326	56 ± 24	33-112
Settled BOD_{21}, mg/L	—	—	108 ± 57	40-246	25.4 ± 12.7	12.2-59.5
Volatile phenol, mg/L	7.5 ± 1.8	5.3-10.6	2.19 ± 1.64	0.34-5.0	0.1 ± 0.05	0.05-0.25
Total phenol, mg/L	26.4 ± 5.3	16.7-34.4	12.6 ± 4.7	6.6-23	4.1 ± 1.3	2.3-7.6
Ash content of activated sludge, %	—	—	13.9 ± 5.0	8.5-24.8	10.3 ± 1.8	8.0-13.4
Sludge volume index, mL/g	—	—	77 ± 19	50-115	79 ± 22	43-108
Average hydraulic residence time, hrs	—	—	6.8		20.4	
Mixed liquor suspended solids under aeration*4, mg/L			1000-1500		2000	
Treatment stage sedimentation tank underflow solids*4, mg/L			2000-4000		5000-6000	
Estimated food-to-microorganism ratio (sludge loading), mg BOD_7/mg MLSS-d			0.14		0.07	
Estimated sedimentation tank hydraulic loading, m^3/d/m^2			34.6		15.5	
Estimated sedimentation tank solids loading, kg/hr/m^2			2.36		2.49	
Estimated sludge recycle, m^3/d			20,860*5		20,400	

N o t e s : *1 Total indicates parameter was measured with suspended solids present.
*2 First-stage biological process experiences 208 ± 71 mg/L suspended solids in the sedimentation basin overflow.
*3 Settled indicates parameter was measured after solids were separated by gravity.
*4 Information provided by L.I. Korolenko, Manager of Kohtla-Järve WWTP.
*5 Includes 8590 m^3/d of underflow activated sludge from second-stage biological treatment process.

Once the various wastewater sources are blended in the Kohtla-Järve facility equalization basins, the combined wastewater is directed to activated sludge treatment for removal of soluble and insoluble organic constituents found in the individual waste streams. Treated effluents from the second-stage activated sludge sedimentation tanks are discharged via a pipeline and deep-water outlet to the Gulf of Finland. Waste sludge dewatering and digestion is not performed at the wastewater treatment facility. The waste sludge is pumped to a nearby waste disposal area directly from the sedimentation tanks.

The treatment performance of the existing biological treatment system at Kohtla-Järve indicates that the activated sludge process is adversely impacted by the high solids carry-over associated with the operation of the second-stage activated sludge sedimentation tanks. The current data indicate that removals of BOD_7 and COD from the combined municipal and industrial wastewaters were 81 % and 49 %, respectively, with effluent suspended solids present in the sample, but improved to 91 % for BOD_7 and 70 % for COD when the suspended particulate was removed from the treated effluent. Similar results were also determined for measured BOD_{21} and phosphorus in the combined municipal and industrial wastewaters [2]. It is conceivable that if the effluent suspended solids were reduced to concentration levels consistent with the requirements of the Helsinki Commission for the Baltic Sea as stipulated by the "Helcom Recommendations" (i.e., 15 mg/L TSS), the existing WWTP could possibly also meet the allowable effluent requirements for BOD_7 and total phosphorus. However, this premise must be examined in light of the additional waste pollutant and hydraulic loads that will be associated with the future regional wastewater treatment facility at Kohtla-Järve. The existing biological WWTP is not effective at nitrification of influent ammonia. Treatment plant performance indicates that the majority of the nitrogen removed by the process is associated with microorganism maintenance (i.e., biomass synthesis), and less than 32 % of the remaining ammonium-nitrogen undergoes conversion to nitrites and nitrates [2]. There also may be possible inhibitory effects on biological nitrification associated with the presence of phenolics in the Kiviter and Kiviõli wastewaters, as evidenced by the presence of high residual nitrite concentrations in the treated effluents. The literature indicates that phenol present in the activated sludge process mixed liquor above 5.0 mg/L will inhibit ammonia oxidation by bacteria [3, 4].

Table 1 presents data which describes the influence of treatment stage on the performance of the existing biological treatment process and indicates that approximately 24 % of the total BOD_7 and 60 % of the settled BOD_7 is removed across the first-stage of the Kohtla-Järve activated sludge process. Removals of volatile and total phenols averaged approximately 71 % and 52 %, respectively, in the first-stage of the

biological process [2]. It may be that suspended particulates in the effluents of the first-stage activated sludge sedimentation tanks also impacted the treatment performance of this process [2]. However, it is also true that this condition results from a low active biomass under aeration and a relatively short hydraulic residence time in the first-stage biological process, all other parameters not withstanding. The overall treatment performance of the Kohtla-Järve activated sludge process also was adversely impacted by the damaged condition of the fine-bubble porous diffuser system in several of the biological reactors (i.e, aeration basins).

The existing aeration basins consist of four reaction compartments or bays which are arranged for plug or series flow of wastewater and return activated sludge. Traditionally, a plug flow tank geometry is used to meet the mixing and oxygen transfer requirements of diffused aeration systems applied to the treatment of municipal wastewaters. As one of its characteristics, the plug flow configuration has a high organic loading at the influent end of the aeration basin. Loading is then reduced over the length of the aeration basin as the organic components of the wastewater are assimilated by the microorganisms. At the downstream end of the basin, oxygen consumption primarily results from endogenous respiration. However, this arrangement is not the actual configuration of the existing activated sludge process presently operated at Kohtla-Järve. Under the existing arrangement, the first bay of each reactor receives all the return activated sludge, while the influent wastewater enters the second and third bays through a distribution trough that divides the flow evenly within the available basin volume. These conditions create the following process-related deficiencies when treating the combined municipal and industrial wastewaters at Kohtla-Järve.

• Because the return activated sludge enters the process independent of the incoming wastewater, a condition of sludge stabilization (i.e., aerobic digestion) is produced that may result in a reduction of microbial activity and a lessening of the treatment of the various dissolved constituents present in the industrial wastewater sources.

• Introducing 50 % of the influent wastewater into the third bay of the biological treatment reactor results in a shortening of the overall hydraulic residence time (HRT) of the process. This has the effect of providing less time for effective treatment, and the subsequent removal of the more persistent constituents in the wastewaters is reduced.

Because of its shortened HRT and low mixed liquor suspended solids (MLSS) concentration, the Kohtla-Järve biological wastewater treatment process is more sensitive to changes in hydraulic and/or BOD_7 loadings. These sensitivities have resulted in diminished performance, and noncompliance with the "Helcom Recommendations".

Table 2. **Waste Loadings for Regional Wastewater Treatment Plant at Kohtla-Järve**

Wastewater Sources	Flow, m^3/d	BOD_7, kg/d	COD, kg/d	Total phosphorus, kg/d	Total nitrogen, kg/d	Suspended solids, kg/d	Volatile phenols, kg/d	Total phenols, kg/d
Municipal wastewaters								
Kohtla-Järve	14,040	967	3,313	38	407	1,264	3.10	23
Kohtla-Nõmme	405	79	243	1.01	12	105	0.97	5.75
Ahtme	8,400	2,470	4,940[*1]	57	307	1,277	0.22	--
Jõhvi	7,500	2,955	5,910[*1]	43	254	915	0.12	--
Kukruse	135	22	44[*1]	0.28	2.55	7.15	0.01	--
Kiviõli	4,020	346	868	16	105	273	0.04	12
Total municipal	34,500	6,839	15,318	155.29	1087.55	3841.15	4.46	40.75
Industrial wastewaters								
Kiviter tar removal	8,500	4,000	9,350	3.5	94	850	300	600
Kiviter dephenolization	1,000	2,000	3,500	0.5	400	50	70	500
Kiviõli oil shale plant	1,500	1,020	2,500	4.0	60	225	30	225
Nitrofert	3,250	250	750	5.0	680	750	--	--
Velsicol Eesti AS:								
Benzoic acid[*2]	810	325	550	--	121	41	1.1	4.3
Benzoate esters[*3]	65	4,255	6,450	--	--	--	--	4.3
Kiviõli industries	400	500	800	--	--	--	--	--
Püssi PPK[*4]	1,580	1,300	3,200	6.5	47	224	1.2	--
Kohtla-Järve power plant	900	30	200	1.0	6	80	--	--
Total industrial	18,005	13,680	27,300	20.5	1,408	2,220	402.3	1333.6
Spent shale pile runoff	2,500	1,000	3,750	0.75	62.5	500	87.5	175
Total wastewater loads	55,005	21,519	46,368	176.54	2558.05	6561.15	494.26	1549.35

Notes: [*1] Estimated from BOD_7/COD equal to 0.5.
[*2] Waste loads adjusted for future benzoic acid production of 54,545 metric tons per year.
[*3] Estimated from information provided by Velsicol Eesti AS for the new benzoate esters plant wastewaters.
[*4] Town of Püssi and Mining pits of Aidu included with particle board manufacture wastewater.

Kohtla-Järve Wastewater Loadings

The waste loadings for the future regional wastewater treatment plant at Kohtla-Järve are presented in Table 2. The future wastewater treatment plant will process 55,005 m^3/d of wastewater with an average BOD_7 loading of 21,519 kg/day and a suspended solids loading of 6,561 kg/day. This is a flow increase of 76 % over the current average WWTP dry weather hydraulic loadings, and a 236 % increase in the current BOD_7 loads. Future total phosphorus and total nitrogen loadings will equal 177 kg/day and 2,558 kg/day, respectively. The future wastewater will provide all of the phosphorus and nitrogen needed for biomass synthesis, which will result in an 85 % reduction of the overall waste total phosphorus and a 42 % reduction of the total nitrogen load under average conditions. The projected wastewater chemistry of the future Kohtla-Järve WWTP suggests that the "Helcom Recommendations" for allowable effluent total phosphorus may possibly be met by biomass synthesis requirements alone. However, an additional 33 % removal of the influent wastewater, total nitrogen level may also be required to meet future "Helcom Recommendations" for the discharge of treated effluents to the Gulf of Finland. The future volatile phenol and total phenol loadings will equal 494 kg/day and 1,550 kg/day, respectively. This is a 110 % increase in the volatile phenol and an 88 % increase in the total phenol loadings on the existing wastewater treatment system at Kohtla-Järve [2].

The regional WWTP will receive 63.6 % of its future BOD_7 loading from industrial wastewater sources, with Kiviter/Kiviõli oil shale operations accounting for more than half of this pollutant load. Kiviter/Kiviõli oil shale operations will account for 33.1 % of the overall COD pollutant load and 17.2 % of the suspended solids load on the future regional WWTP [2]. Typical compounds identified in oil shale sour condensate [5] are presented below:

Phenol	Piperidines
Ortocresol	Anilines
Metacresol	Indans
Paracresol	Tetralins
2,6-Dimethylphenol	Naphthalenes
2,3,5-Trimethylphenol	Tetrahydroquinolines
Methylisopropylphenol	Quinolines
2,4-Dibutylphenol	Indoles
Pyrocatechol	Hydrocarbons
Methylresorcinol	PNAs
2,5-Dimethylresorcinol	Carbazoles
Substituted benzenes	Tetramines
Pyridines	

These data indicate that, in addition to phenolics, the organic compounds present in oil shale sour condensate are nitrogen-containing species, the predominant types being pyridines and anilines.

The Kiviter/Kiviõli facilities are responsible for 81 % of the volatile phenol and 85.5 % of the total phenol loading on the future Kohtla-Järve WWTP. This suggests that an improvement in dephenolization operations at the facilities would benefit the overall operation of the wastewater treatment system. However, most of the volatile phenol is derived from the Kiviter tar removal operations, which do not now have unit processes for the treatment of phenol-bearing wastes [2]. Nevertheless, the existing activated sludge process at the regional WWTP has demonstrated considerable effectiveness for the degradation of the phenolic compounds in the Kiviter wastewater. It is well established that most monohydric and polyhydric phenols experience complete degradation by heterotrophic bacteria during aerobic biological treatment [6, 7].

Industrial wastewater sources from the Velsicol Eesti AS facility at Kohtla-Järve are estimated to contribute 21.3 % of the BOD_7 loading on the regional WWTP. The future benzoate esters production unit will produce glycol benzoates, such as esters of diethylene glycol and dipropylene glycol. The production facility is a batch process where esters of dipropylene glycol are produced 80 % of the time [2].

Industrial wastewater sources will be responsible for 55.0 % of the future total nitrogen load on the regional WWTP, with wastewaters from Nitrofert operations accounting for approximately 50 % of the industrial nitrogen load [2]. Ammonia and carbon dioxide are the principal dissolved gases in the industrial wastewaters. With the Kiviter/Kiviõli oil shale operations wastewaters, these gases probably originate during the retorting operation while other inorganic constituents such as carbonates and bicarbonates originate from contact between the retort water and raw or spent shale in the retort. The "Helcom Recommendations" will require that the regional wastewater treatment facility not only achieve biological nitrification of the combined municipal and industrial wastewaters, but also that it maintain effective biological denitrification operations in the activated sludge process while simultaneously treating high levels of influent carbonaceous BOD_7. In its present process configuration, the Kohtla-Järve biological WWTP would not be capable of maintaining this degree of nitrogen removal.

Single Sludge Activated Sludge Systems

To comply with more stringent effluent requirements, the functions of the Kohtla-Järve activated sludge system must be expanded to perform simultaneously the biological removal of carbon, nitrogen, and

phosphorus. This expansion will increase the complexity of the system configuration and, concomitantly, the number of biological processes that must be sustained to effect a given effluent quality.

Experience has shown that a conventional, plug-flow activated sludge reactor can be easily converted to a biological nutrient removal process by establishing an anaerobic zone at the influent end and creating a series of anoxic and aerobic zones through the process, as illustrated by the schematic layouts presented in Fig. 1. One approach recommended for improvement of the Kohtla-Järve wastewater treatment system specified the use of the five-stage Bardenpho™ process to meet the future carbon, nitrogen, and phosphorus discharge limitations stipulated by the "Helcom Recommendations." The traditional Bardenpho™ process consists of a series of four anoxic and aerobic zones following an anaerobic reactor, with recycling of mixed liquor from the first aerobic zone to the first anoxic zone at a rate as high as four to six times the influent flow rate. The process configuration is intended to achieve more complete nitrogen removal than is possible with a two- or three-stage process. However, complete denitrification cannot be attained with preaeration anoxic zones alone because part of the aerobic stage effluent is not recycled through the anoxic zone. It is the second anoxic zone which provides for the additional denitrification using nitrate produced in the aerobic stage as the electron acceptor and endogenous organic carbon as the electron donor [8-10].

In principle, the second (post-aeration) anoxic zone is capable of almost complete removal of nitrate in the aeration tank effluent. The final aeration stage in the Bardenpho™ process strips residual gaseous nitrogen (N_2) from solution and minimizes phosphorus release in the final clarifier by increasing the oxygen concentration. The ability to successfully employ the Bardenpho™ process to achieve an effluent concentration low in total nitrogen depends on the ratio of oxidizable nitrogen to carbon in the influent to the activated sludge process [11].

A modification of the five-stage Bardenpho™ process that eliminates the recycle of nitrates in the return activated sludge to the anaerobic zone is the modified University of Cape Town (UCT) process [12, 13]. This process, which is shown schematically in Fig. 1, provides for protection of the anaerobic zone from the detrimental effects of nitrates on phosphate removal performance.

These processes accomplish an apparent expansion of the activated sludge system through changes in system configuration and microbial metabolism. The objective is to establish the environmental conditions in the activated sludge system that are conducive to the optimal growth and performance of microorganisms that naturally achieve carbonaceous BOD removal, nitrification, denitrification, and biological excess

phosphorus removal. These diverse mixed cultures of microorganisms are described in Table 3 [12].

To achieve biological nutrient removal, an activated sludge system must contain three microorganism groups: ordinary heterotrophs which are unable to accumulate polyphosphates; polyP heterotrophs (i.e., phosphorus accumulating microbes); and autotrophs which mediate nitrification [14-16].

Table 3. **Microorganism Groups for Biological Removal of Carbon, Nitrogen, and Phosphorus [12]**

Biological process	Zone
Ordinary heterotrophs (unable to accumulate polyphosphates)	
COD removal (organic degradation)	Aerobic
Ammonification (organic N; NH_4^+)	Aerobic
Denitrification (organic degradation; NO_3^-; NO_2^-; N_2)	Anoxic
Fermentation (F-RBCOD; SCFA)	Anaerobic
PolyP heterotrophs (accumulate polyphosphates)	
Phosphorus release (SCFA uptake; PHA storage)	Anaerobic
Phosphorus release (SCFA uptake; PHA storage)	Anoxic
Phosphorus uptake (PHA degradation)	Anoxic
Phosphorus uptake; phosphorus removal (PHA degradation)	Aerobic
Autotrophs (nitrifiers)	
Nitrification (NH_4^+; NO_2^-; NO_3^-)	Aerobic

Notes: F-RBCOD - Fermentable readily biodegradable COD.
       SCFA - Short-chain fatty acids.
       PHA - Polyhydroxy-alkanoates.

The biological uptake and removal of phosphorus by the activated sludge process is "in excess" of the normal metabolic requirements for microorganism growth. In this process, the amount of phosphorus incorporated in the sludge is increased from the normal level of approximately 0.03 mg P/mg VSS to values between 0.06 and 0.15 mg P/mg VSS. This is achieved by stimulating the growth of polyP microorganisms which store large quantities of phosphorus internally as polyphosphates [17-19]. This is accomplished through the use of an anaerobic/aerobic sequence of biological reactors and the presence of short-chain fatty acids (SCFA) in the anaerobic reactor. In such a system, both the ordinary heterotrophs and the polyP heterotrophs exist contemporaneously. The larger the population of polyP microbes, the greater the percentage of phosphorus uptake by the activated sludge and, consequently, the larger the amount of phosphorus removed from the wastewater. The relative proportion of the two microorganism groups in the activated sludge depends on the fraction of the influent wastewater biodegradable COD that each group can utilize.

Nitrification Inhibition and Toxicity

There are numerous constituents in the industrial wastewater sources at Kohtla-Järve that are inhibitory to nitrifying bacteria (e.g., *Nitrosomonas* sp.). Constituents such as the phenolics present in the Kiviter and Kiviõli industrial wastewaters; the methanol, diethylene glycol, and dipropylene glycol present in the Velsicol Eesti AS industrial wastewaters; and solvents, glues, and resins that may be present in the industrial discharges from Püssi PPK (i.e., particle board manufacturer). These constituents can inhibit ammonia-nitrogen oxidation by activated sludge. The quantification of toxicity in biological treatment systems is difficult, due to a number of factors that may also affect nitrification rates. These include temperature, pH, dissolved oxygen concentration, and organic constituent loading. There are also sorption effects and the compounding effects when more than one toxic compound is present in the industrial wastewater [11, 20-23].

Ammonia biooxidation also is inhibited by the free ammonia (NH_3) concentration in wastewater which is a function of pH and temperature as depicted in Fig. 2.

Depending on pH, free ammonia concentrations in the range of 10 to 150 mg/L will result in the inhibition of *Nitrosomonas* [24, 25]. *Nitrobacter* is inhibited at free ammonia concentrations of 0.1 to 1.0 mg/L and free nitrous acid concentrations of 0.2 to 2.8 mg/L [26].

Fig. 2. Distribution of ammonia and ammonium ion with pH and temperature

The levels of free ammonia and free nitrous acid in a given wastewater are a function of pH and ammonium and nitrite concentrations. Table 4 presents the ranges of ammonium-nitrogen and nitrite-nitrogen concentrations as a function of pH where *Nitrobacter* may be inhibited.

Single sludge biological nutrient removal activated sludge systems treating municipal wastewaters typically remove all biodegradable COD in the
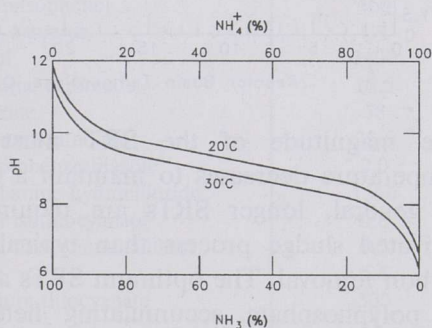
Table 4. **Ammonium-Nitrogen and Nitrite-Nitrogen Concentrations for Nitrobacter Inhibition, mg/L**

pH*	NH_4^+- N range	NO_2^-- N range
6.0	210-2100	30-330
6.5	70-700	88-1050
7.0	20-210	260-3320
7.5	7-70	—
8.0	2-20	—

Note: * - Temperature = 20 °C.

anaerobic and anoxic zones, resulting in ideal growth conditions for nitrifiers in the aerobic zone [13]. Therefore, higher specific nitrification rates should occur in the aerobic zone of a biological nutrient removal system than in a fully aerobic conventional activated sludge system treating the same municipal wastewater at the same solids retention time (SRT).
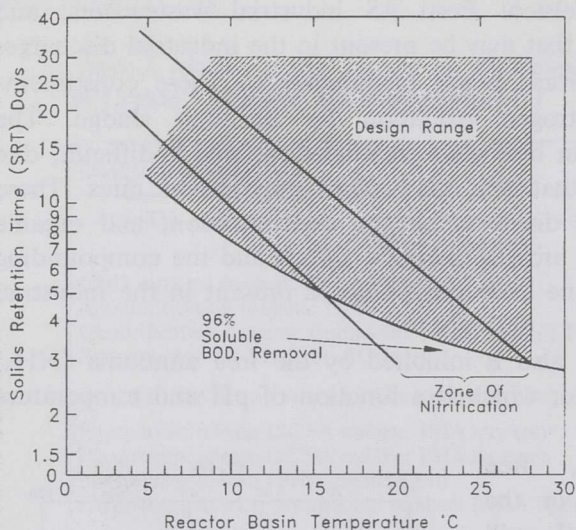

Fig. 3. Solids retention times for carbonaceous BOD removal and nitrification

The design SRTs which are optimum for the development of both heterotrophic and autotrophic bacteria in an activated sludge process are dependent on the operational reactor (aeration) basin temperatures (Fig. 3).

The magnitude of the SRT must increase as the aeration basin temperature decreases to maintain a stable biological treatment process. In general, longer SRTs are required to achieve nitrification in an activated sludge process than typically are needed to achieve organic carbon removal. The optimum SRTs are also shorter for the development of polyphosphate accumulating heterotrophs in an activated sludge process [12]. This is attributed to the low observed endogenous decay rate of the polyP bacteria, which is about 0.05 day^{-1} as opposed to 0.24 day^{-1} for normal heterotrophic microorganisms [13].

Bardenpho^{TM} and other single-sludge biological nitrification-denitrification processes were developed primarily for the removal of nitrogen from municipal wastewaters (i.e., sewage). These processes have not been successfully applied to the treatment of industrial wastewaters of the type produced by RAS Kiviter or Velsicol Eesti AS. There does not now exist a functional commercial-scale industrial wastewater treatment facility which is using the Bardenpho^{TM} process or some variation of this process in the treatment of its wastewaters. The anaerobic first-stage of the Bardenpho^{TM} process is not consistent with the removal of high concentrations of difficult-to-degrade, organic compounds from industrial wastewaters. The achievement of a high degree of inhibitory organic compound removal in the first-stage of the process is a necessary

condition to ensure effective nitrification in subsequent stages of the process. The selection of this biological treatment process for industrial wastewater treatment without first conducting pilot-scale tests to verify its performance could result in system failure due to activated sludge toxicity, particularly with regard to biological nitrification.

Organic compounds that inhibit nitrification are presented in Table 5 [4]. These data indicate that the most severely toxic organic compounds to *Nitrosomonas* are sulfur compounds such as thiourea, thiosemicarbazide, and thioacetamide. Blum and Speece [27] developed IC_{50} values for a laboratory *Nitrosomonas* culture exposed to a number of inhibitory organic compounds. Their research indicated that most monohydric and polyhydric phenols were inhibitory to *Nitrosomonas*.

It is generally acknowledged that nitrification rates in two sludge activated sludge reactors are greater than those in

*Table 5.* **Organic Compounds that Inhibit Nitrification [4]**

Compound	Concentration at 75 % inhibition, mg/L
Acetone	2000
Allyl alcohol	19.5
Allyl chloride	180
Allyl isothiocyanate	1.9
Benzothiazole disulfide	38
Carbon disulfide	35
Chloroform	18
o-Cresol	12.8
Diallyl ether	100
Dicyandiamide	250
Diguanide	50
2,4-Dinitrophenol	460
Dithio-oxamide	1.1
Ethanol	2400
Guanidine carbonate	16.5
Hydrazine	58
8-Hydroxyquinoline	72.5
Mercaptobenzothiazole	3.0
Methylamine hydrochloride	1550
Methyl isothiocyanate	0.8
Methyl thiuronium sulfate	6.5
Phenol	5.6
Potassium thiocyanate	300
Skatol	7
Sodium dimethyl dithiocarbamate	13.6
Sodium methyl dithiocarbamate	0.9
Tetramethyl thiuram disulfide	30
Thioacetamide	0.53
Thiosemicarbazide	0.18
Thiourea	0.076
Trimethylamine	118

single sludge fully aerobic conventional reactors because the organic matter has been removed in the first stage, and there is less heterotrophic competition in the second stage. Research by Hanaki, et al. [28, 29] clearly demonstrated that the presence of biodegradable organics inhibited ammonia oxidation, apparently because of competition from growing heterotrophic microbes. Nitrite oxidation was not inhibited. They also showed that low dissolved oxygen concentrations will substantially increase the growth yield of ammonia oxidizers, which compensates for

reduced specific substrate utilization rates at low dissolved oxygen. However, the nitrite oxidizers are strongly inhibited at dissolved oxygen concentrations below 0.5 mg/L.

Biological Denitrification

Two modes of nitrate reduction can occur in microbial processes: assimilating and dissimilating or denitrification. Assimilating nitrate reduction results in the reduction of nitrate to ammonia for use in microorganism synthesis. It occurs independent of oxygen concentration and when ammonia-nitrogen is not available to the bacteria. Dissimilating nitrate reduction or denitrification is coupled to the respiratory electron chain and results in the reduction of nitrates to nitrite to nitric oxide to nitrous oxide to nitrogen as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
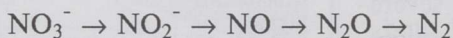
Denitrification is an anoxic process, occurring in the absence of oxygen, and requires an organic or inorganic electron donor to proceed. Neither biological nitrogen removal nor biological phosphorus removal can be accomplished without sufficient biodegradable organic substrate (i.e., RBCOD or BOD). Although the rates of denitrification are affected by the specific organic compounds available in the wastewater, approximately 8.6 mg COD/L of municipal wastewater is needed to reduce 1.0 mg/L of nitrate-nitrogen to nitrogen gas [30].

A dissolved oxygen concentration of 0.2 mg/L and above has been reported to inhibit denitrification of a *Pseudomonas* culture for activated sludge treating domestic sewage [31]. The fraction of the biomass exposed to anoxic conditions depends on the bulk liquid dissolved oxygen concentration, the floc size, and the organic and ammonia loadings which affect respiration rates. Besides the effect of dissolved oxygen on the initiation of denitrification, the oxygen concentration in the mixed liquor may also impact the denitrification rate. An important operating consideration in nitrogen removal systems is the time required for the bacteria to activate or deactivate their nitrate reductase enzyme at the end of the electron transport respiratory chain. As with all enzymatic reactions, pH influences the denitrification rate. Alkalinity is produced in heterotrophic denitrification reactions and the pH is generally elevated, instead of being depressed as in nitrification reactions. One equivalent of alkalinity is produced per equivalent of nitrate-nitrogen reduced, or one-half the amount destroyed when ammonium is oxidized to nitrate.

Denitrification kinetics is impacted by whether a single-stage or multiple-stage pre-anoxic zone is used in the process (Fig. 1). A mass balance on the organic substrate should be developed prior to

determining the organic substrate removal rate. The relationship between organic substrate consumed and nitrate-nitrogen reduction is used to determine the nitrate reduction rate due to bacteria synthesis, substrate removal, and endogenous decay. This approach is analogous to that employed to determine oxygen requirements in a biological process for heterotrophic substrate removal [1]. The rate equation generally takes the form:

$$R_{no} = f(R_{su}, K_d, Y, F_{dn})$$

where R_{no} is the nitrate reduction rate

R_{su} is the substrate removal rate

K_d is the endogenous decay coefficient

Y is the synthesis yield coefficient

F_{dn} is the fraction of heterotrophic microorganisms consuming nitrate

The accuracy of using this approach to modeling nitrate reduction is dependent on the values of the various coefficients and parameters in the equation. Estimating the F_{dn} value is compounded by the fact that facultative, strictly aerobic, and possibly strictly anaerobic populations can exist contemporaneously in the activated sludge process. The substrate utilization rate may also vary for a facultative population of microorganisms when nitrate is used as the electron acceptor instead of oxygen. Because of the difficulty of separating these critical kinetic parameters, empirical relationships have been developed to describe a specific denitrification rate in pre-anoxic zones of biological nutrient removal systems.

Biological Phosphorus Removal

The effect of SRT on phosphorus removal is complex. The relationship between SRT and phosphorus removal as a function of the anaerobic mass fraction (i.e., mass of sludge in anaerobic zone per total mass of sludge in the activated sludge process) is presented in Fig. 4a. These data which were developed from a steady-state model for biological excess phosphorus removal [12] indicate that for SRTs less than 3.0 days, the phosphorus removal increases with increasing SRT. However, for SRTs greater than 3.0 days, the phosphorus removal decreases with increasing SRT. The data also indicate that phosphorus removal increases with increasing anaerobic mass fraction. This is due to increased conversion of F-RBCOD to SCFA with larger anaerobic mass fractions. The apparent improvement in phosphorus removal diminishes with each step increase in the anaerobic mass fraction because the conversion follows first-order

kinetics. The F-RBCOD consumption during biological phosphorus removal varied from 35 to 70 mg COD per mg P removed from municipal wastewater.
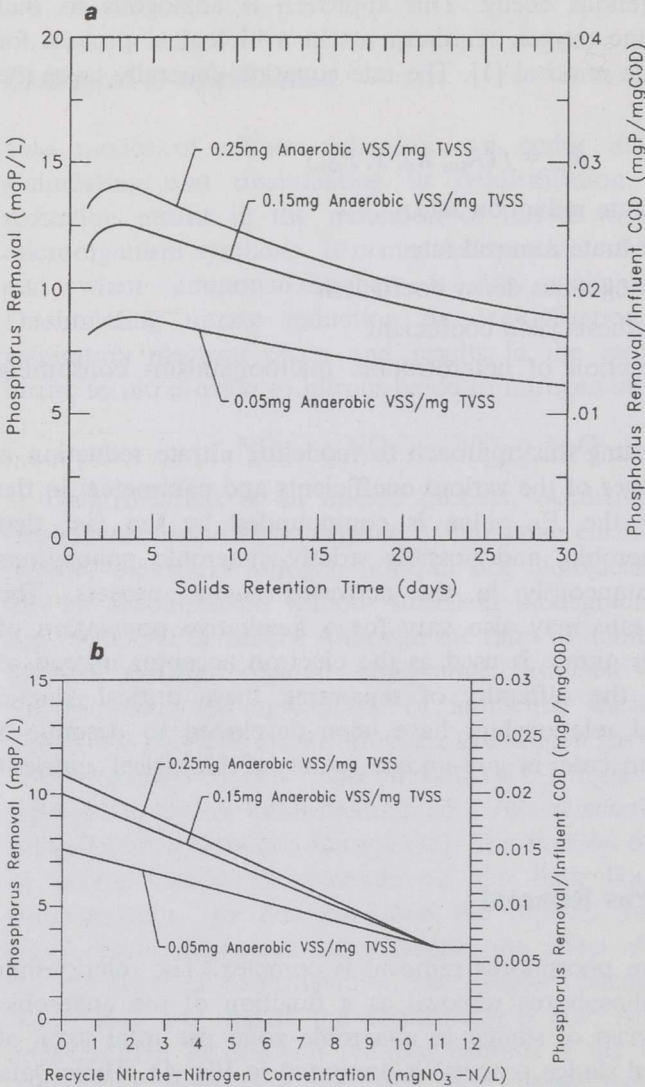

Fig. 4. The variation of phosphorus removal with (*a*) solids retention times and (*b*) recycle nitrate-nitrogen concentration for biological excess phosphorus removal systems

An increase in the SRT can cause an increase in the population of ordinary heterotrophs which, in turn, cause an increase in F-RBCOD removal, with subsequent increases in P release and P uptake. However, an increase in the process SRT can also cause a decrease in P uptake because of the lower population of polyP bacteria wasted per day. At SRTs less than 3.0 days, the former dominates the P removal; while at SRTs greater than 3.0 days the latter dominates, giving rise to the shape

of the curves in Fig. 4*a*. These effects are influenced by the specific endogenous decay rate of the polyP bacteria. The data presented in Figure 4*a* indicate that biological excess phosphorus removal is optimum at SRTs between 3 and 5 days. However, to achieve nitrification, the activated sludge process SRTs should be greater than 10-15 days, depending on the anaerobic mass fraction, reactor basin temperature, and the specific growth rate of the nitrifier population. Obviously, there are constraints on a biological nutrient removal system for the optimization of both nitrification and excess phosphorus removal which result from the operational sludge age of an integrated single sludge activated sludge system.

The impact of recycling mixed liquor containing nitrate-nitrogen to the anaerobic stage of the biological nutrient removal system is illustrated in Fig. 4*b*. These data indicate that the recycling of nitrate has a markedly deleterious influence on the magnitude of phosphorus removal by a biological nutrient removal system. As the nitrate-nitrogen concentration in the mixed liquor recycle to the anaerobic reactor increases, the apparent phosphorus removal decreases. This negative impact on phosphorus removal is more pronounced with increasing anaerobic mass fraction. This results from a lower rate of rejection of SCFA to the bulk liquid, and the subsequent increase in the utilization of the fatty acids for growth and energy with nitrate as an electron acceptor by ordinary heterotrophic bacteria. Therefore, allowing nitrate to enter the anaerobic reactor will reduce the mass of SCFA available to the polyP bacteria, and correspondingly reduces the potential phosphorus removal of the biological nutrient removal system. The lower boundary on phosphorus removal presented in Figure 4*b* results from wastage (at a SRT of 20 days) of activated sludge with normal metabolic phosphorus content (i.e., 0.03 mg P/mg VSS).

Conclusions

The modified Bardenpho™ and other single-sludge biological nutrient removal processes were developed primarily for the removal of nitrogen and phosphorus from municipal wastewaters (i.e., sewage). These processes have not been successfully applied to the treatment of industrial wastewaters of the type produced by RAS Kiviter or the other industries in the Kohtla-Järve region of Estonia. There does not now exist a functional commercial-scale industrial wastewater treatment facility which is using the Bardenpho™ process or some variation of this process in the treatment of its wastewaters. Therefore, the selection of this biological treatment process without first conducting pilot-scale tests to

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verify the performance of this technology in this application is not recommended.

There are numerous constituents in the industrial wastewater sources at Kohtla-Järve that are inhibitory to nitrifying bacteria (e.g., *Nitrosomonas* sp.). Constituents such as the phenolics present in the Kiviter and Kivioli industrial wastewaters; the methanol, diethylene glycol, and dipropylene glycol present in the Velsicol Eesti AS industrial wastewaters; and solvents, glues, and resins that may be present in the industrial discharges from Püssi PPK (i.e., particle board manufacturer). These constituents can inhibit ammonia-nitrogen oxidation by activated sludge.

The anaerobic first-stage of a single-sludge biological nutrient removal process is not consistent with the removal of high concentrations of difficult-to-degrade, inhibitory organic compounds from industrial wastewaters. The achievement of a high degree of inhibitory organic compound removal in the first-stage of the treatment system is a necessary condition to ensure effective nitrification in subsequent stages of the process. The use of single-sludge nitrification-denitrification processes are generally inappropriate for the treatment of complex industrial wastewaters. These wastewaters usually require the application of aggressive aerobic biological treatment for organic carbon removal so that ammonia oxidation can be accomplished without suppression of the nitrifier population by inhibitory organic compounds present in the industrial wastewaters.

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