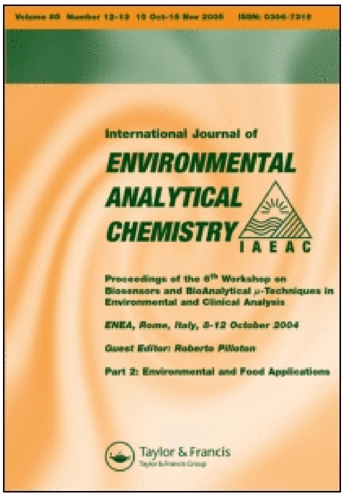

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Speciation Efficiency Indices (SEI) and Readily-Biodegradable Indices (RBI) for Optimising Ligand Control of Environmental and Associated Industrial Processes

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SPECIATION EFFICIENCY INDICES (SEI) AND READILY-BIODEGRADABLE INDICES (RBI) FOR OPTIMISING LIGAND CONTROL OF ENVIRONMENTAL AND ASSOCIATED INDUSTRIAL PROCESSES

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Two new concepts, termed Speciation Efficiency Index (SEI) and Readily-Biodegradable Index (RBI) have been introduced as markers of the efficiency of agents to form a species and to biodegrade, when applied to process-specific roles; these are illustrated using data from two industrial-environmental studies.

Chelating agents such as EDTA and DTPA have been employed in many industrial and environmental processes to sequester specific metal ions that have deleterious effects upon the process itself. These two agents do not comply with the most recent international criteria for ready-biodegradability. Hence, several chelating agents (*S,S'*-EDDS, IDS and NTA) have been assessed in terms of their SEI, using the Joint Expert Speciation System, with particular reference (a) to replacing EDTA in the pulp and paper-making industry, and (b) to judge the transuranic decontamination effects of EDTA, *S,S'*-EDDS, NTA and citrate in the nuclear industry.

For both pulp processing and for radionuclide decontamination, both SEI and RBI values lead to the conclusion that the best agent is *S,S'*-EDDS.

Keywords: Speciation Efficiency Index; Chemical Speciation Simulation; Cheating agents; JESS program; Readily-Biodegradable Index; *S,S'*-EDDS

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INTRODUCTION

Before the introduction of computers into chemical researches in 1955, the concept of the "effective" or "conditional" stability constant was introduced to better represent the ability of ligands to complex with metal ions [1]. In particular, the protonation constants of the ligands and the hydrolysis characteristics of the metals in solution were embodied.

Many of today's researchers and authors of sales literature still attempt to correlate effectiveness with the 1 : 1 conditional stability constants.

Half a century later, the modern approach uses computer speciation simulation programs, which are based upon many thousands of individual chemical species, and large databases of metal–ligand–proton thermodynamic data (K_{MLH}), and has had remarkable success in correlating biological, environmental or industrial effects with individual chemical *species* concentrations rather than with *total* amounts.

Furthermore, original modelling concerns about slow equilibria, and about macromolecules such as proteins and lignins affecting metal ion binding, have been allayed by concepts such as ion buffering control, and outputs as a relative percentage rather than absolute values [2].

This paper introduces new concepts for chemical speciation simulation researches into industrial and environmental processes, demonstrates their applicability and stresses the importance and significance of evaluating and applying "Speciation Efficiency Indices" (SEI) for reporting and interpreting data from speciation-based studies.

Next, with the implementation of agreements such as OSPAR [3], which include zero-emissions for man-made chemical substances, the monitoring of chemical emissions into the environment to ensure good housekeeping, and the introduction of more environmental-friendly agents, indices are used to objectively assess the biodegradation properties of these chelating agents.

SPECIATION EFFICIENCY INDEX (SEI)

There are now many scenarios in which speciation qualitatively correlates with effect. Our new concept of quantifying these relationships is to introduce an index. Of the many examples illustrating the use of these indices, we describe two which involve assessing the influence of industrial use of EDTA upon environmental sustainability.

EDTA was first introduced in 1935, and has had remarkable success as a chelating agent since then. However, with increased environmental awareness and specific concerns over environmental fate of polyamino-carboxylates (Table I), coupled with the introduction of legislation such as OSPAR [3], EDTA is being replaced in those roles which emit to the environment.

Environmental Fate of EDTA

In 1990, the OECD initiated a study to investigate the physiochemical properties, environmental fate, ecotoxicity and toxicity of High Production Volume (HPV) chemicals (i.e. those reported to be either produced by, or imported into, at least one EU country at levels greater than 1000 tonnes per annum), as there is a much greater likelihood of environmental accumulation, than of low production volume chemicals. These data are presented as SIDS (Screening Information Data Sets). Clearly, EDTA is a HPV chemical, with an estimated 200,000 tonnes (including NTA) being produced worldwide, each year.

Progress in this area has been slow; this led to an announcement by the International Council of Chemical Associations (ICCA) in 1998 that some 1000 "priority" chemicals out of a list of more than 4000 HPV chemicals, would have complete SIDS sets by the end of 2004 [4].

EDTA and its sodium salts are one of the chemicals on the current ICCA HPV working list (it is included in Annex A (1999) which has been published in addition to the main list of 1000 priority chemicals) [4]. It appears that although full SIDS assessments for EDTA and its sodium salts are not complete at this present time, a SIAR assessment (SIDS Initial Assessment Report) has been completed [4], and much is already known about the environmental fate of EDTA.

Table I shows a summary of some recent literature reports [5–19] that describes the environmental fate of EDTA. All of the EDTA-elimination routes described in these reports involve *specific*, often *extreme*, conditions. EDTA is not considered to be "readily-biodegradable" under general environmental conditions and fails the ready-biodegradability criteria set by OECD.

Thus, worldwide, there is a considerable amount of activity in finding readily-biodegradable replacement ligands which in chelation terms are as good as, or better than EDTA [20–26] and which satisfy the OECD "ready-biodegradability" data.

TABLE I Statements from a literature survey of the degradation of EDTA. The exact quotations, and conditions of the experiment, are given in the references listed

	Reference
The recalcitrance of EDTA towards biodegradation in wastewater treatment or in the environment has directed much attention to other elimination mechanisms	5
Contradictory results have been published concerning the biodegradation of EDTA. Biodegradation is a minor route; abiotic processes are mostly responsible for it's elimination.	6
In conventional biological wastewater treatment plants, EDTA is neither degraded by microorganisms nor activated sludge. No biodegradation has been detected in OECD tests	7, 8
Biochemical and photochemical degradations do not eliminate the environmental impact of metal-complexed EDTA because of the slow degradation. It is recommended that the use of EDTA be minimised wherever possible until an effective means for its removal has been developed. Another approach would be to use less calcitrant ligands as sequestering agents.	9
EDTA is predominantly eliminated *via* photodegradation. However, only Fe(III)EDTA is susceptible to sunlight irradiation, whereas other environmentally related EDTA species (Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) will not directly photolyse.	6
Abiotic photodegradation appears to be restricted to the Fe–EDTA complex and is dependent upon the degree of sunlight upon the localised environment. On cloudy days, no significant decreases in EDTA concentrations were observed in a Swiss River, but all the available Fe–EDTA was photodegraded under sunny conditions	5
Direct photodegradation, advanced oxidation by metal (hydr)oxides, and sorption by particles, followed by sedimentation, are important processes for the partial elimination of EDTA from aquatic systems	6
Photolysis clearly does not result in the total mineralisation of EDTA, but forms more easily biodegradable metabolites, which still have metal complexing properties. After 6.5 hours, irradiation of Fe–EDTA complex with sunlight forms ED3A, EDDA and EDMA. This mixture of photolysis metabolites was incubated with activated sludge and a bioelimination of 53% was observed within 4 weeks	6, 10
ED3A, one of the metabolites of EDTA photodegradation may itself be persistant. Further research should also focus upon on AOP metabolites themselves.	6, 10
Certain Abiotic Oxidative Processes (AOP) have been used upon synthetic effluents containing EDTA. EDTA was effectively removed by O_3/UV treatment at $pH = 7.0$	11
Mineralisation of EDTA may be achieved by mixed cultures	12
Pure culture (*Agrobacterium radiobacter*) were able to degrade Fe(III)–EDTA at concentrations exceeding 100 mmol dm^{-3}	6, 13
Pure bacterial isolates, BNC1 and DSM9103 were able to degrade EDTA	6, 14, 15
EDTA may be metabolised by activated sludge through an ED3A (ethylenediaminetriacetate) intermediate into more readily-biodegradable components, IDA (iminodiacetate) and iminoacetaldehyde	16
EDTA may be removed by absorption by iron or aluminium (hydr)oxides in which EDTA is sorbed to the sediment	5, 17, 18
EDTA may be removed by abiotic oxidation with Mn(III/IV)oxides, yielding ED3A and EDDA.	6, 19

All of these *desiderata* are chemical speciation-dependent, but there is the related challenge of how we reconcile sometimes competing data in an objective manner. We suggest that the use of SEI can resolve these issues.

Defining the Index

The Speciation Efficiency Index (SEI) of an agent is a value (assessed in terms of chemical speciation of metal–ligand–proton equilibria) which reflects its efficiency at a particular pH at successfully satisfying all the criteria of success aimed for within a particular (chelation) process.

SEI values allow objective intercomparison studies between several different agents which are being considered, for example, as replacement agents for an industrial process, and allows potential process developers to select new agents based upon their desirable speciation properties.

Two examples which address the use of SEI for assessing the efficiency of chelating agents in industrial processes, are the replacement of EDTA in pulp processing and of EDTA in radionuclide decontamination operations. These two examples have been selected from our current researches into environment-friendly chelating agents, since the gap left by the failure of EDTA to satisfy international criteria in terms of biodegradability and, in certain cases, in terms of chelation efficiency, in the absence of biodegradable replacement agents, could considerably damage many industries. It is noteworthy that the worldwide usage of EDTA in the pulp and paper industry is estimated to be in the region of some 15,000 and 20,000 metric tonnes per annum.

METHODS AND RESULTS

The SEI Concept in Environmental Protection

(a) Replacement Agents for EDTA in the Pulp and Paper Industry

Consider the following three interdependent speciation schemes:

i. EDTA is used to sequester transition metal ions, principally Mn, Fe and Cu ions, during the paper-making process in order to inhibit the generation of radical species at the hydrogen peroxide bleaching stage, which are though to cause problems during processing and in the quality and brightness of the end-product [27–31];

ii. Magnesium ions are required during pulp processing to ensure product strength and ideally ought not to be greatly complexed by the ligand added to remove the above transition metal ions [27–31];
iii. Further, some of the ligand can be distracted by binding to calcium ions present in pulp, thus detracting from the efficiency of the ligand, and so requiring more ligand to be added.

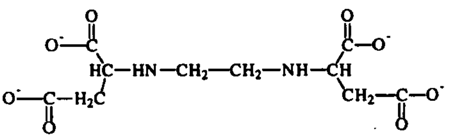
Thus, computer simulations illustrating the propensity of the individual chemical reactions between metal ions present in pulp and complexing agents were constructed to reflect the metal-ion speciation under the typical conditions of pulp-making (Table II). The reactions of the agents *S,S'*-EDDS, EDTA, NTA and IDS (Fig. 1) were simulated using the JESS program and database. Their corresponding SEI values are given in Figs. 2–5. *The higher the value of the SEI, the more efficient the agent.*

The JESS program [32–34] is a thermodynamics-based chemical equilibrium modelling program which identifies the quantitative chemical speciation in a specific system under investigation. The calculations are performed by a series of interactive commands and sequences which are solved using Newton–Raphson style iterative mathematics. The species distributions are based upon both the total concentrations of basic components (i.e. metals and ligands) and on the propensity of the formation constants (metal–ligand–proton) for the individual reactions. The JESS database contains 210,000 critically assessed log K values for 71,000 individual chemical reactions, and is one of the most extensive and validated databases available.

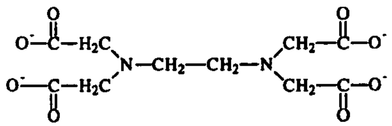
For this pulp-making process, three separate indices relating to the three interdependent speciation schemes described earlier in this section, are added together. The overall index (the SEI value) is an objective measure

TABLE II Concentration of components in pulp (10% slurry consistency) in a typical pulp processing stage

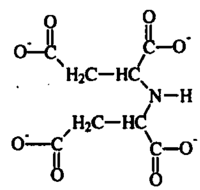
Component	*Concentration* (mol dm^{-3})
Ba	9.3×10^{-6}
Ca	3.5×10^{-3}
Cu	6.3×10^{-6}
Fe	2.3×10^{-5}
Mg	1.1×10^{-3}
Mn	6.5×10^{-5}
Zn	8.0×10^{-6}
Sulphate	1.7×10^{-3}
Chelating agent (EDTA or new agent)	6.8×10^{-4}



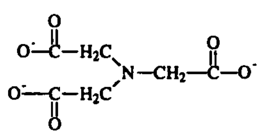
S,S'-Ethylenediaminedisuccinate (*S,S'*-$EDDS^{4-}$)



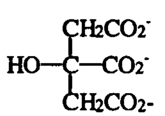
Ethylenediaminetetraacetate ($EDTA^{4-}$)



Iminodisuccinate (IDS^{4-})



Nitrilotriacetate (NTA^{3-})



Citrate (Cit^{3-})

FIGURE 1 Structures of some of the chelating agents discussed in this paper.

of the ability of the ligand to completely sequester the problem transition metals ions, to leave magnesium uncomplexed, and to avoid being "distracted" through complexing to calcium ions present Eq. 1).

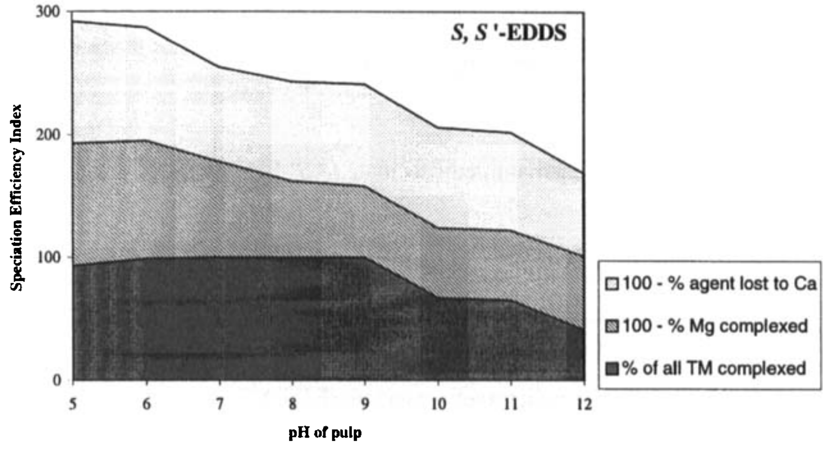


FIGURE 2 Speciation Efficiency Index profile for *S,S'*-EDDS in pulp processing.

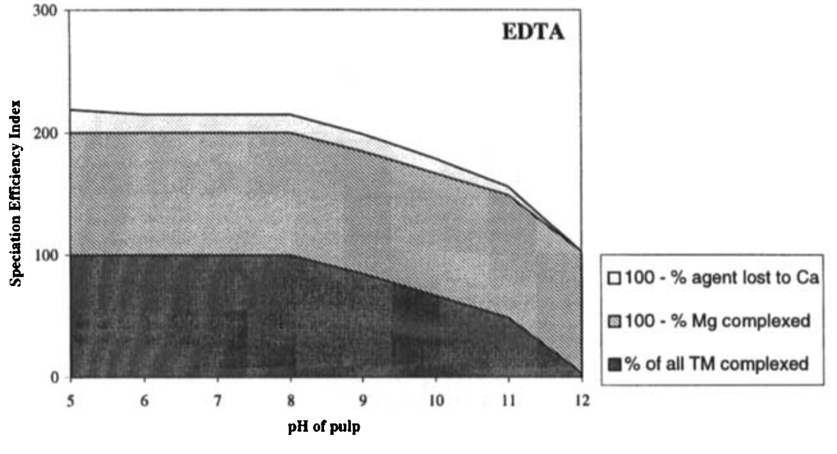


FIGURE 3 Speciation Efficiency Index profile for EDTA in pulp processing.

$$\begin{aligned}\text{SEI for pulp treatment} = &\ \%\ \text{total Mn, Cu, Fe complexed} \\ &+ (100 - \%\ \text{Mg complexed}) \\ &+ (100 - \%\ \text{ligand agent lost to Ca}) \qquad (1)\end{aligned}$$

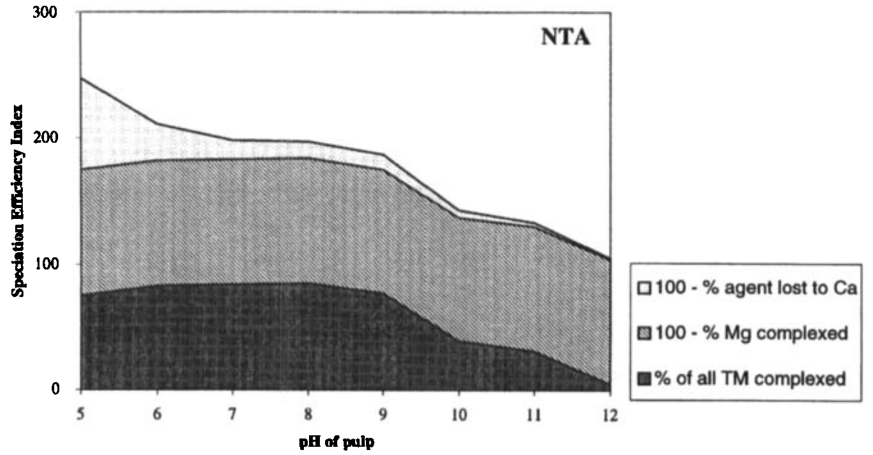


FIGURE 4 Speciation Efficiency Index profile for NTA in pulp processing.

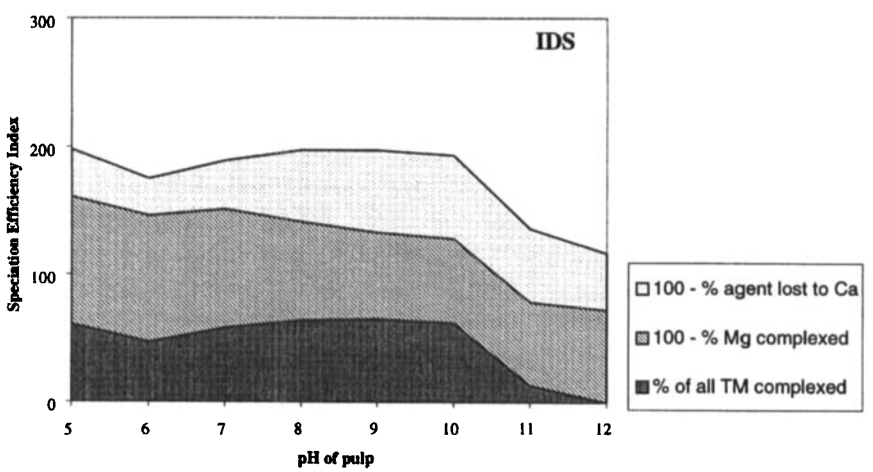


FIGURE 5 Speciation Efficiency Index profile for IDS in pulp processing.

For the *standard* pulp processing conditions simulated (i.e. a simple 1:1 replacement of EDTA with new agent), clearly *S,S'*-EDDS is far superior to all three other agents, since it is 100% efficient at complexing the transition metal ions and avoids the calcium complexing more than EDTA. However, this means there is more ligand left over to complex some of the magnesium.

Depending upon *specific* concentration data for a given pulp process which are raw material (wood and water supply) dependent, optimised SEI could easily be generated for each specific plant, which also counteracts using the new agent in excess thus complexing the magnesium.

Such plots also permit one to observe pH effects; *S,S'*-EDDS is totally effective at transition metal ion binding up to pH = 9, whereas EDTA begins to lose efficiency above pH = 8.

(b) Replacement Agents for EDTA-based Decontamination Formulations used in the Nuclear Industry

EDTA-based decontaminating formulations are used extensively throughout the nuclear industry to sequester transuranics and other fission products. Previously, we have reported the use of the JESS program to simulate the chemical speciation of typical nuclear waste stream components (radioactive components: Pu^{4+}, Am^{3+}, $UO_2{}^{2+}$, $NpO_2{}^{+}$, Sr^{2+}, Cs^{+}, Sb^{3+}, Co^{2+}, Mn^{2+}, Ru^{4+}, Ce^{3+}, Eu^{3+}; non-radioactive components: Fe^{3+}, Cr^{3+}, Ni^{2+}, Mg^{2+}, Zr^{4+}, Mo^{3+}, Gd^{3+}, Nd^{3+}) from a decontamination process using *S,S'*-EDDS, EDTA, and citrate, to assess the degree of complexing of these components by ligand [35]. In this paper, we turn our attention to Speciation Efficiency Indices applied to these agents and additionally for NTA, for decontaminating plant items and waste-stream (Table III).

The SEI for decontamination has been defined in Eq. (2), as the percentage of total 'radioactive' components sequestered by the complexing agents, allowing much better objective evaluations of the effectiveness of the agent. Although the SEI values for decontamination do not list non-radioactive ion species, these were accounted for in the speciation simulations, i.e. radioactive ions complexed, in the presence of non-radioactive ions.

$$\begin{aligned}\text{SEI for radionuclide decontamination}\\ = \%\ \text{radioactive actinides complexed}\\ + \%\ \text{radioactive lanthanides complexed}\\ + \%\ \text{radioactive transition metals complexed}\\ + \%\ \text{radioactive main group metals complexed}\end{aligned} \tag{2}$$

SEI clearly show that *S,S'*-EDDS is as good as EDTA at complexing the *radioactive* components at pH = 7 and 9, and may be better than EDTA at more alkaline pH values. The SEI values also show that the pH values for maximum decontamination are 5 for EDTA and 7 for *S,S'*-EDDS.

TABLE III The percentage of *radioactive* actinides (Pu^{4+}, Am^{3+}, UO_2^{2+}, NpO_2^{+}), lanthanides (Ce^{3+}, Eu^{3+}), main group metals (Sr^{2+}, Cs^{+}, Sb^{3+}), and transition metals (Co^{3+}, Mn^{2+}, Ru^{4+}) complexed by the ligand S,S'-$EDDS^{4-}$, NTA^{3-}, $Citrate^{3-}$ or $EDTA^{4-}$, and their corresponding pH dependent Speciation Efficiency Indices (SEI). *Percentage of non-radioactive ions are not shown in this table, but were included in our speciation simulations.*

Ligand	*pH*	*% actinides complexed by ligand*	*% active lanthanides complexed by ligand*	*% active main group metals complexed by ligand*	*% active transition metals complexed by ligand*	*SEI*
S,S'-$EDDS^{4-}$	**5**	99	100	42	65	**306**
	7	99	100	64	66	**329**
	9	72	100	69	66	**307**
	11	53	100	82	66	**301**
NTA^{3-}	**5**	91	100	35	65	**291**
	7	75	100	56	66	**297**
	9	50	100	66	66	**282**
	11	50	100	66	65	**281**
$Citrate^{3-}$	**5**	99	100	49	62	**310**
	7	100	100	58	65	**323**
	9	75	100	67	66	**308**
	11	50	100	78	66	**294**
$EDTA^{4-}$	**5**	100	100	66	81	**347**
	7	100	100	66	70	**336**
	9	75	100	64	66	**305**
	11	74	100	57	66	**297**

Citrate also appears to have a similar efficacy as *S,S'*-EDDS in the higher pH region. However, NTA is far less efficient at complexing the *radioactive* components over the complete pH range from 5 to 11 (Figure 6).

The Use of Readily-Biodegradable Indices (RBI) for Agent Assessment

Biodegradation may be defined as "the metabolism of organic chemicals by heterolysic microorganisms to form microbial biomass and simple inorganic and organic products such as carbon dioxide and methane" [36].

Fundamentally, biodegradability of chemical agents may be illustrated by Eq. (3).

$$\text{agent} + O_2 \rightarrow CO_2 + H_2O + \text{biomass}. \tag{3}$$

Chelating agents such as EDDS and IDS, or specific isomers of these agents, are biodegradable, having been assessed in terms of the OECD guidelines [37]. A wide array of tests and criteria are used to assess the biodegradability of chemicals and the results of these tests are frequently used in sales litera-

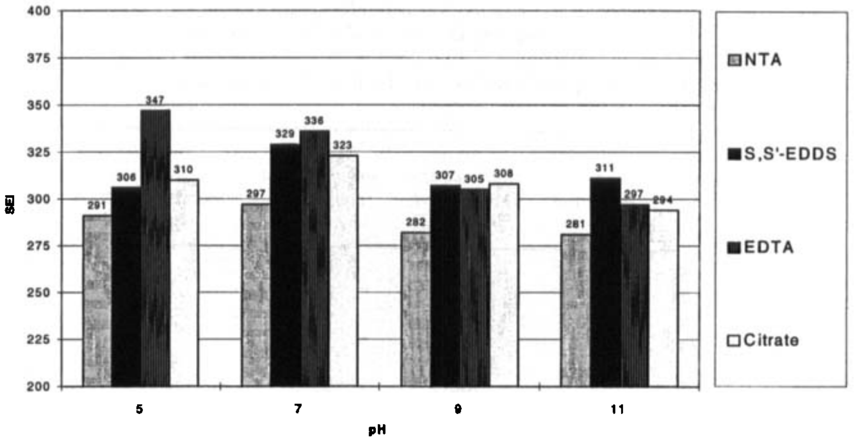


FIGURE 6 Speciation efficiency indices for NTA, *S,S'*-EDDS, EDTA and citrate for active radio nuclide decontamination.

ture to market new products, and to allay environmental concerns. Terms such as "readily-biodegradable" and "inherently-biodegradable" are frequently used to describe those chemicals which have been assessed and which pass the OECD 301 and 302 tests respectively [37]. Each test is further sub-classified into OECD 301 test A to E and OECD 302 test A, B and C; the most common tests used to assess ready-biodegradability are the OECD 301B (also called the modified Sturm) test [37] and the OECD 301E (called the modified screening) test [37].

Chelating agents are comprised from the elements carbon, nitrogen and oxygen, and the tracking of the fates of these agents in terms of these components is often used as a measure of the degree of biodegradation, e.g. the Dissolved Organic Carbon (DOC) levels, the Biochemical Oxygen Demand (BOD), or the carbon dioxide production (based upon the theoretical carbon dioxide production, $ThCO_2$). Thus, the tests for ready-biodegradability are most frequently based upon the levels of DOC (OECD 301E) or the percentage of $ThCO_2$ produced (OECD 301B).

The OECD guidelines stipulate that "the pass levels for ready-biodegradability are 70% removal of DOC and 60% of ThOD or $ThCO_2$ production". "Those pass levels have to be reached in a 10-day window within the 28-day period of the test". "The 10-day window begins when the degree of biodegradation has reached 10% DOC, ThOD or $ThCO_2$, and

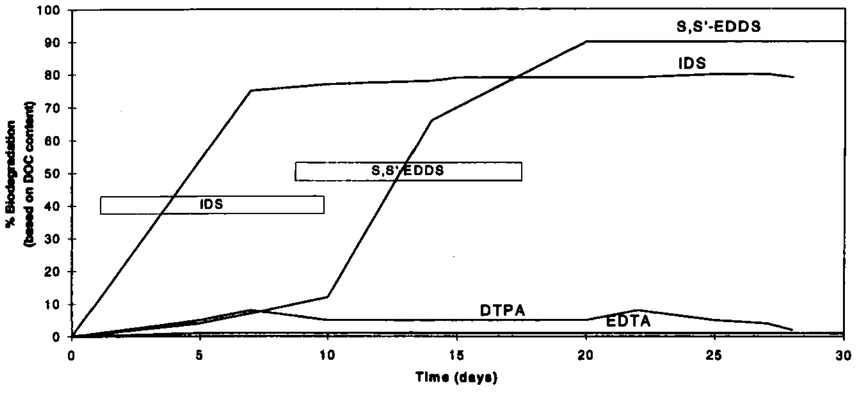


FIGURE 7 Biodegradability profiles (OECD 301E) for *S,S'*-EDDS, IDS, EDTA and DTPA. The boxes indicate the 10 day screening window which refers to the OECD criterion, agent must achieve 60% more biodegradation in 10-days.

must end before day 28 of the test. Chemicals which reach the pass levels after the 28 day period are not deemed to be readily-biodegradable" [37].

The pass levels are lower in OECD 301B compared with OECD 301E (i.e. 60% $ThCO_2$ compared with 70% DOC) since some of the carbon from the agent will form new biomass, thus rendering the percentage of CO_2 lower than the percentage of carbon being used [37]. Ultimately, agents assessed using either OECD 301B or OECD 301E should, in theory, produce similar biodegradability profiles (according to Eq. (3)), due to the laws of physical science, i.e. matter cannot be created or destroyed, but can interconvert from one chemical species to another.

We have surveyed a selection of publications and promotional literature [38–43] and attempted to produce a single chart showing the biodegradability profiles of some of the chelating agents in this paper (Fig. 7). Generally, these biodegradability profiles can be divided into three distinct phases, the "lag period", the "degradation phase" and the "plateau phase" [44].

Thus, we propose that in addition to our SEI concept, another index, that of Readily-Biodegradable Indices (RBI) be used.

The RBI of an agent is expressed as a percentage score. There are two criteria involved in scoring: (i) the percentage reported is the plateau percentage reached within 28 days of test initiation, provided that, (ii) to qualify for this plateau score, within the overall 28 days, once the degradation has reached 10% a further 50 or 60% (OECD 301E, or OECD 301B tests respectively) must biodegrade within the following ten day interval; otherwise the score is set at 0%.

We have tested the data distributed by Manufacturers against the above criteria and assigned RBI values for the ligands; *S,S'*-EDDS (90%), IDS (80%), EDTA (0%) and DTPA (0%). It is clear that only *S,S'*-EDDS and IDS pass the OECD criteria for ready-biodegradability. In fact, EDTA and DTPA do not reach the initial 10% commencement of biodegradation, and thus have an RBI score of 0%.

We have been unable to fully consider NTA in our studies, since a definitive biodegradability profile is not available; there is much confusion in the literature arising from non-OECD references to NTA. BASF report that "NTA is readily-biodegradable under environmental conditions" and "NTA's potential to biodegrade was open to question for many years" [41]. Tuulos-Tikka *et al.* reported that "NTA degrades well in normal waste water" but does not mention the term *readily*-biodegradable [21]. Canton and Stoof report that NTA does undergo biodegradation as "the percentage of DOC decreases by more than 80% within four weeks" [42]; these data are 20 years old, and the OECD guidelines have been modified several times since their publication. A study by Means *et al.* concluded that "long-term biodegradation rates decreased in the order NTA > EDTA = DTPA" [43].

Citrate, along with aspartic acid and other fundamental carboxylic acids, is often the product of biodegradation of more sophisticated ligands, and thus the literature contains no details of the subsequent biodegradation of citrate.

CONCLUSIONS

This paper has amply illustrated the value of efficiency indices based upon (i) chemical speciation data from well verified and validated computer simulations of highly complex chemical systems, and also upon (ii) published data converted to RBI for assessing the ready-biodegradability status of agents.

Such indices facilitate the logical planning of researches, lead to the design of new agents and add order to laboratory evaluations. These factors can substantially improve ligand choice, risk-based environmental impact statements, and ensure maximum safety. Furthermore, such indices are relatively inexpensive to determine given the widespread availability of software and databases which has followed Schubert's conditional constants of 1955.

Other more subjective criteria may be added to these objective assessments; for example, supplier preference, price, patenting etc. can be added in order to create an extremely useful management tool for comparing purchase *prices* with environmental *costs*.

These efficiency indices enable research managers to embody all considerations into one overall index by adding weightings according to their subjective impressions. Meanwhile, the scientists whose work is being directed can be assured that all aspects have at least been included in the judgements.

In summary, for pulp-making, although the best EDTA replacement agents are IDS and *S,S'*-EDDS, having similar RBI scores, SEI evaluations show that *S,S'*-EDDS outperforms the others. For radionuclide decontamination, based upon SEI, both *S,S'*-EDDS and citrate are more or less equivalent to EDTA in terms of efficacy. However, where as EDTA has an RBI = zero, for *S,S'*-EDDS, the RBI is 90%.

The Speciation Efficiency Indices (SEI values) assigned for ligands in the pulp-processing and radionuclide decontamination industries are based upon theoretical models of the prevailing thermodynamic equilibria. Such data ought to be validated through experiments performed in conjunction with both the pulp and paper, and the nuclear, industries.

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