13

LIST OF FIGURES (slides) and TABLES

INTRO – Sorption and Biosorption

Figure i-1	The two phenomena differ only in the type of the solid sorbent material employed			
Figure i-2	Concentration gradient is the driving force for sorption and also biosorption			
Figure i-3	In actual applications biosorbents would go inside conventional sorber equipment to do the job			
Figure i-4	Expertise and collaboration of several disciplines is required to develop an interdisciplinary topic			
Figure i-5	Leonardo Da Vinci			
Figure i-6	Individual parts are available – please communicate			

1 – POTENTIAL OF BIOSORPTION

Figure 1-1	Unearthed metals mobilized by man represent a threat as they concentrate in the food chain			
Figure 1-2	Conventional techniques for removing dissolved heavy metals metals from solution			
Figure 1-3	Biosorption is competitive and cheap			
Figure 1-4	Advantages of biosorption would tend to outweigh the very few shortcomings of biosorbents in applications			
Figure 1-5	Number of different metal-sorbing biomass types with different properties have been identified			
Figure 1-6	Biosorption emerges as a new technology for removing heavy metals. It is based on development and formulation of new biosorbent materials			
Figure 1-7	There are risks involved in introducing new technologies			
Figure 1-8	For treating effluents, small-scale treatability tests are necessary			
Figure 1-9	Treatability studies provide a basis for assessing the process feasibility			
Figure 1-10	There may be a broader basis for a business venture based on an effluent treatment process			
Figure 1-11	The enterprise based on biosorption can span a broad range or a selected specific part of it			
Figure 1-12	A conservative estimate for a biosorption enterprise niche market			
Figure 1-13	Technological, economic and organizational aspects need to be thoroughly developed			
Figure 1-14	There are potential partners - and better ones			
Figure 1-15	Pure gold ?			

2 – BIOSORPTION R&D

Figure 2-1	Biosorption has a promise, particularly enormous in environmental applications			
Figure 2-2	Application areas for biosorption clean-up			
Figure 2-3	Screening for new biosorbents is essential			
Figure 2-4	Using waste microbial biomass for preparing new biosorbents is particularly advantageous			
Figure 2-5	Promising biosorbents have been reported			
Figure 2-6	Use common sense when looking for biosorbent materials: They have to be sorbing well, inexpensive, easily available, processed and used in a process. Understanding the biosorption mechanism makes it easier to look for high-sorbing analogues			
Figure 2-7	Biosorption is a relatively new and developing field			
Figure 2-8	Some advice for screening			
Figure 2-9	Equilibrium sorption is the basis for SCREENING			
Figure 2-10	Preliminary sorption tests should be carried out with good understanding of sorption equilibrium principles – they are explained in Chapter 6.1			
Figure 2-11	Advance from simple to more complex sorption systems. There are practically NO "single-metal systems" – there are always other ions in solution !			
Figure 2-12	Electronmicrographs of different patterns of uranium (a) [38], and thorium (b) [37] deposition in the cell wall of <i>Rhizopus arrhizus</i> fungus at pH 4 (electron-dense dark areas)			
Figure 2-13	Equilibrium contact experiments lead to establishing a series of "final concentrations" and corresponding (calculated) "uptakes" – serving as a basis for the sorption isotherm plot that, in turn, serves as the basis for the isotherm plot			
Figure 2-14	Comparing sorbents A and B through the sorption isotherm plot. In this case, in the low-concentration region A is better, then B is better. Only in simpler cases, would one isotherm as a whole lie above the other			
Figure 2-15	ADSORPTION capacity is examined first			
Figure 2-16	Studying biosorption systems			
Figure 2-17	Standard procedure for evaluating simple sorption systems - it is detailed in Chapter 6			
Figure 2-18	Fixed-bed column is the most effective and common sorption process arrangement			
Figure 2-19	The sorption column behavior is complex			
Figure 2-20	Batch or CSTR contactor-reactor			
Figure 2-21	Opposite to the uptake (sorption), DESORPTION leads to regeneration of the sorbent and to the eventual recovery of sorbate			
Figure 2-22	Things to watch for when looking for a suitable solution to elute the sequestered sorbate (metal)			
Figure 2-23	The sorbate is released at lower pH of the sorption system. Acid wash could thus be used for (metal) desorption			
Figure 2-24	Concentration of the sorbate in the effluent eluate is important for its further recovery (or disposal)			
Figure 2-25	Biosorbent Solids to eluting Liquid ratio (S/L) is of importance to overall process effectiveness too			
Figure 2-26	Complete sorbent regeneration may take two or more operations, usually "in situ" in the column			
Figure 2-27	Understanding the MECHANISM of (bio)sorption is important even for very practical reasons			
Figure 2-28	Chemical binding as well as physical deposition of microprecipitates may be taking place			
Figure 2-29	The predominant active binding site depends on solution conditionsconditions – e.g. solution pH affects their availability			
Figure 2-30	In MODELING - advanced scientific approach aids in understanding the phenomenon and in developing biosorption for applications			
Figure 2-31	Process modeling is sophisticated and should be done very pragmatically			

Figure 2-32	Contemporary molecular modeling software is extremely powerful and can be very useful		
Figure 2-33	GRANULATION is an essential 'process development' type of work essential for flow-through column sorption applications and studies		
Figure 2-34	Laboratory R&D on biosorbent granulation presents logistical challenges		
Figure 2-35	Different biomass types require different 'pre-processing' after which the sorption performance has to be always tested		
Figure 2-36	The gel of biosorbent itself or the entrapping gel may be relatively "transparent" for small species of the sorbent (like metal ions)		
Figure 2-37	In process development work it is mandatory to keep in mind the feasibility of the WHOLE sorption process as it is applied		
Figure 2-38	Correspondingly, there is a number of different process aspects to be optimized. Some may be more important than others		
Figure 2-39	Different areas of the project can benefit most from specific scientific disciplines		
Figure 2-40	Challenges for chemistry and biochemistry		
Figure 2-41	Process engineering will have to develop the process with its 2 types of pilots		
Figure 2-42	Seaweeds can becollected wild or 'sea-farmed'. Some brown kelp can grow almost 25 cm/day		
Figure 2-43	(R&D) More detailed discussion of granulation procedures and processing is in Chapter 9		
Table 2-	-1 Biosorbent uptake of metals by microbial biomass - partial compilation		

3 - BIOSORPTION MECHANISM

Figure 3-1	Microbial metal accumulation has been known for decades. Biosorption adds a new challenge and dimension to the phenomenon.		
Figure 3-2	While any or combination of these metal sequestering mechanisms may be active, ion exchange often dominates.		
Figure 3-3	Binding by complexation		
Figure 3-4	Example of copper complexation		
Figure 3-5	Complex formation - stoichiometric relationships		
Figure 3-6	Some coordinating groups		
Figure 3-7	Common chemical groups amenable to hydrogen replacement		
Figure 3-8	The principle of ion exchange		
Figure 3-9	The principle of adsorption		
Figure 3-10	With microprecipitation the sorbate is deposited in clusters and filtration may gain predominance		
Figure 3-11	Knowledge is important !		
Figure 3-12	As biosorption is mainly by ion exchange, different types of (bio)sorbents are required		
Figure 3-13	There are three major ways how pH can influence metal biosorption		
Figure 3-14	lonic strength suppresses the primary uptake		
Figure 3-15	Example of Cr-V interference		
Figure 3-16	Sorption binding forces		
Figure 3-17	Competition in ion exchange can be used to drive the desorption process – mainly with protons. Beware of studying desorption in a batch mode !		
Figure 3-18	Adsorption and microprecipitation		
Figure 3-19	Instrumental analyses helpful in investigating biosorption deposition of metals		
Figure 3-20	Alginate has carboxyl groups on its monoblocks: M – manuronic and G- guluronic acids		
Figure 3-21	Examples of FTIR spectra of Fe-loaded Sargassum biomass [20]		
Figure 3-22	The overall structure of the carboxyl group bound to metal (M) in a chelating form		
Figure 3-23a	FTIR analyses of blank and Cr-loaded AWUS biosorbent (top curve)		
Figure 3-23b	FTIR spectrum of pure chromium trioxide		
Figure 3-24	FTIR spectra of blank AWUS and V-loaded AWUS biosorbent (top curve)		

Figure 3-25 Figure 3-26	FTIR spectra of Au-loaded AWUS biosorbent Schematic concept of anion binding on chitin-based biosorbent			
Table 2.	Table 2.1 Fundamentals of sorption methods			
Table 2.	Table 2.2Major binding groups for biosorption			
Table 2-3:Carboxyl stretching frequencies for different forms of Sargassum biomass				
	<i>Table 2-4</i> (3.3.1.1) [58] Cr adsorption by AWUS: Summary of FTIR spectral data (cm ⁻¹)			
Table2	5 (3.3.1.) V adsorption by AWUS: Summary of FTIR spectral data (cm ⁻¹)			
<mark>4 - BIOSORPTIO</mark>	N OF METAL IONS			
Figure 4-1	Categories of metals of interest for biosorption			
Figure 4-2	Industrial sectors known to discharge heavy metals. Growth industries and point source effluents are of primary concern.			
Figure 4-3	Acid Mine Drainage is a serious and widespread concern associated with mining activities			
Figure 4-4	AMD carries toxic heavy metals and is continuously generated on sites of active as well as decomissioned mines			
Figure 4-5	Acid Mine Drainage stream			
Figure 4-6	Berkeley Pit mine in Butte, Montana, USA, in 1979. Dimensions: 1.5 x 1.0 miles			
Einer 47	opening, 1,700 feet deep. Mining was suspended in 1982			
Figure 4-7	Berkeley Pit mine (in 1995) has been flooding. Steadily rising water level, if not controlled, would reach the underground water table in several years. It is a time bomb.			
Figure 4-8	Schematic diagram of a coal-fired power generating plant			
Figure 4-9	A coal-fired power generating station			
Figure 4-10	Huge quantities of coal are burned daily			
Figure 4-11	In gold recovery, the metal forms a very stable complex with cyanide. Gold-cyanide is an anionic complex.			
Figure 4-12	Since precious and high-value metals are very much worth recovering – the biosorption process could conceivably make a contribution there.			
Figure 4-13	The list of "Rare Earths"			
Figure 4-14	A wide range of new technologies depends on the availability of RREs			
Figure 4-15	Biosorption of Rare Earth Elements may be a useful challenge - for recovery purposes			
Figure 4-16	Approximate prices for Rare Eaths (1998)			
Figure 4-17	Lanthanide complexes in solution			
Figure 4-18	More common "industrial metals" that occur as cations in aqueous solutions			
Figure 4-19	More common "industrial metals" that occur as anions in aqueous solutions			
Figure 4-20	Health hazards associated with exposure to some anionic metals			
Figure 4-21	Very toxic Chromium occurs mainly as two predominant species (MINEQL+ output)			
Figure 4-22	Vanadium in solution could be in many different ionic forms (MINEQL+ output)			
Figure 4-23	Arsenic speciation in solution as it varies with pH			
Figure 4-24	Very simple is the solution chemistry of Selenium			
Figure 4-25	There are quite a few cations of uranium. The uranium example is developed in some detail in the next section			
Figure 4-26	Distribution of uranium hydrolysis products (reproduced from [3]). (1, 0): $UO_2^{2^+}$; (2, 2): $(UO_2)_2(OH)_2^{2^+}$; (3, 5): $(UO_2)_3(OH)_5^{2^+}$.			
Figure 4-27	lonic composition of hydrolyzed uranium ions at pH 4.0. (Obtained from running program MINEQL ⁺ [21], $UO_2^{2^+} + NO_3^- + H_2O + H^+$ system, pH 4.0, multiple run for total concentration.)			
Figure 4-28	Speciation of hydrolyzed ionic uranium: Top mesh: $UO_2^{2^+}$ Middle mesh: $(UO_2^{2^+})_2(OH)_2^{2^+}$ Bottom mesh: $(UO_2^{2^+})(OH)^+$			
Figure 4-29	MINEQL+ computer program is available free as a demo version (or full for US\$ 500) at : <u>http://www.mineql.com/mineql.html</u>			

Figure 4-30 (repeated *Figure 4-22*): Example of the MINEQL+ output graph for speciation of Vanadium in aqueous solution

Table 4-1	Persistent radionuclides more common in water		
Table 4-2	Surface Finishing Market Breakdown		
Table 4-3	Composition of Specific Metal Concentrations present in Station Waste Stream vs in Nature		
Table 4-4	Some characteristics of rare earths [14]		
Table 4-5	Metal recovery priorization		

5 – SORPTION BY BIOMASS

Figure 5-1	Which biomass ??		
Figure 5-2	Sugar-cane bagasse, abundant agricultural residue, has been tested for biosorption		
Figure 5-3	Almond hulls are another "bio-residue"		
Figure 5-4	The units of a chitin polymer molecule		
Figure 5-5	Chitosan is deacetylated chitin		
Figure 5-6	General composition of crab shells		
Figure 5-7	There are tons of waste crab shells available		
Figure 5-8	Binding of the anion on chitin or chitosan		
Figure 5-9	Abundance of seaweeds could be a beach problem		
Figure 5-10	Sargassum growing in a patch by the shore		
Figure 5-11	Sargassum fluitans seaweed		
Figure 5-12	Some brown macroalgae (seaweeds) of particular interest for their metal biosorption capabilities		
Figure 5-13	Schematic representation of algal cell wall		
Figure 5-14	Major algal polysaccharides and their chemical groups of significance to biosorption		
Figure 5-15	Sargassum is abundant in the warm seas around the globe. Sargassum vulgare, accidentally imported from Japan, is now rapidly expanding on the coasts of Europe from Norway to Portugal		
Figure 5-16	Cellulose is a linear polymer of glucose subunits. It is durable and the most ubiquitous plant material		
Figure 5-17	Alginic acid is likely most amenable to biosorption due to the presence and configuration of the guluronic acid moiety		
Figure 5-18	Metallic cations can crosslink and gel alginic acid. The "egg-box" type of linking is mainly in the region of guluronic acid blocks of the alginic acid molecule		
Figure 5-19	Molecular detail of the "egg-box" structure with with calcium crosslinking two guluronic acid regions in alginate strands. Oxygen atoms involved in chelation are marked by red dots.		
Figure 5-20	L-Fucose units in fucoidan are predominantly 1,2 linked with some 1,3 and 1,4 links		
Figure 5-21	Agar		
Figure 5-22	Sulphated polysaccharide (SPS) κ-carrageenan		
Figure 5-23	The cell wall structure of gram-positive bacteria		
Figure 5-24	The cell wall structure of gram-negative bacteria		
Figure 5-25	Peptidoglycan is in bacterial cell walls		
Figure 5-26	Teichoic acid – a component of bacterial cell wall		
Figure 5-27	Composition of one type of a fungal cell wall (Euascomycete)		
Figure 5-28	The formula of glucuronic acid		
Figure 5-29	Some fungi of specific interest to biosorption		
Figure 5-30	Some large-scale industrial uses of fungi		
Figure 5-31	Industrial fermentation plant		
Table 5-			
Table 5-			
Table 5-	-3 Cell wall biomolecules in fungal biomass*		

 Table 5-4
 Composition of cell wall biopolymers in fungi and bacteria

6 – EVALUATION OF SORPTION PERFORMANCE

<mark>6.1 – SORPTION EQUILIBRIUM</mark>

Figure 6.1-1	Adsorption is different from ion exchange		
Figure 6.1-2	The sorbate uptake is obtained from its mass balance		
Figure 6.1-3	Typical single-sorbate isotherms. Which sorbent here is "better"? Yellow or blue?		
Figure 6.1-4	Langmuir model for the sorption isotherm		
Figure 6.1-5	Brunauer-Emmett-Teller sorption isotherm model		
Figure 6.1-6	As an "external factor", pH has to become a "parameter" for the conventional sorption isotherm plot		
Figure 6.1-7	At low C _f 's "A" is better than "B"		
Figure 6.1-8	At high C _f 's "B" is better than "A"		
Figure 6.1-9	q _{max} indicates the 'ultimate' performance		
Figure 6.1-10	Langmuirian " b " relates to affinity between the sorbent and the sorbate (often metal		
ion considered he	ere)		
<i>Figure 6.1-11</i>	Relationship between Langmuirian b and the equilibrium affinity constant K		
<i>Figure 6.1-12</i>	Relationship of Langmuirian and Ion-Exchange equilibrium constants (affinities)		
Figure 6.1-13	Experimental procedure for deriving the sorption isotherm		
Figure 6.1-6 (rep	<i>neated)</i> pH is an external factor and it has to be controlled for standard isotherm experiments – the final, equilibrium pH is the one that matters !		
<i>Figure 6.1-14</i>	For checking, the loaded sorbent solids can be analyzed too but it is usually more complicated. If they could be completely eluted, the desorption liquid could then be analyzed to make sure that the sorbate mass balance closes		
Figure 6.1-15	In the "tea-bag" experiment $C_i = C_f$		
<i>Figure 6.1-16</i>	Example of "% Removal" screening		
<i>Figure 6.1-17</i>	DANGER: The full isotherms do not follow a pattern		
<i>Figure 6.1-18</i>	Wrong conclusion about the sorbents !		
<i>Figure 6.1-18</i>	"% Removal" is only for crude judgement		
Table 6-1 Some sorption isotherm relationships			

6.2 – MULTI-SORBATE SORPTION EQUILIBRIUM

Figure 6.2-1	For binary metal sorption evaluation only the Equilibrium Final Concentrations must be used			
Figure 6.2-2	Do NOT use the C_i of the second ion !!			
Figure 6.2-3	Correct plot but unlikely to be obtained from randomly generated experimental data			
Figure 6.2-4	Example of studying the effect of Cu on the uptake of Cd. Luckily, there are enough same-parameter experimental data points to enable drawing of isotherm curves in this example			
Figure 6.2-5	The performance of an equilibrium binary sorption system can be depicted by a 3-D sorption isotherm surface replacing the simple one-metal sorption isotherm curve			
Figure 6.2-6	Three different (metal) uptakes can be plotted			
Figure 6.2-7	Each surface can be 'cut' by parallel 'isoconcentration planes' of the 'parameter' - the second sorbate ($^2C_f)$			
Figure 6.2-8	The isotherm surface 'cuts' then represent true sorption isotherm curves at a given concentration (${}^{2}C_{f}$) of the secondary sorbate (parameter)			
Figure 6.2-9	RESULT: evaluation of the second metal presence on the uptake of the primary one: $({}^{1}q) = f ({}^{2}C_{f})$.			
Figure 6.2-10	Vice versa: The effect of M1 on the uptake of M2			
<i>Figure 6.2-11</i>	A binary system sorption isotherm surface for the total metal uptake			
<i>Figure 6.2-12</i>	A binary Fe-Cd biosorption system: The total uptake 3D plot and its 'cuts'. This configuration is not very informative. Look at the next two 3D diagrams.			
Figure 6.2-13	A binary Fe-Cd biosorption system: The effect of Fe on Cd uptake by Sargassum			
<i>Figure 6.2-14</i>	A binary Fe-Cd biosorption system: The effect of Cd on Fe uptake by Sargassum			

6.3 – MODELING OF EQUILIBRIUM SORPTION

Figure 6.3-1	For approximating the binary metal biosorption isotherms in the 3D rendering a simple model was used based on Langmuir isotherm		
Figure 6.3-2	Unsatisfactory curves result from unsmoothed and interpolated-only 3D isotherm surface mesh plots of scattered experimental data. The smoothing of such surface plot needs to be done just like for the usual experimental curve plotting		
Figure 6.3-3	Some isotherm models for ideal sorption systems were introduced in Section 6.1. Further outline of less simplistic models is in this Section		
Figure 6.3-4	From the simplistic Langmuirian approach, modeling of equilibrium sorption progresses to include multicomponent systems, ion exchange with different stoichiometries, different binding sites and the key environmental factors (e.g. pH, ionic strength)		
Figure 6.3-5	Conventional multicomponent Langmuir model with competing ionic species - case (a). This one-site model reflects the 1:1 stoichiometry		
Figure 6.3-6	This combined adsorption-ionex 2:1 stoichiometry requires development of a composite model. The way the stoichiometry is perceived is important for the ease of handling further work with the model and the calculations involved		
Figure 6.3-7	Excess electrical energy possessed by ions due to their surrounding ion clouds is responsible for the deviation of solutions of electrolytes from ideality. Therefore, the activity of ions rather than the concentration should be considered		
Figure 6.3-8	Inside a solid particle. However, a gel particle is likely too look and behave quite differently. From the perspective of a very small species such as a simple metal ion gel may be like water		
Figure 6.3-9	Electrical Double Layer: Gouy-Chapman model lacks the compact (cation) layer assumption		
Figure 6.3-10	Electrical Triple Layer: Stern-Grahame model		
Figure 6.3-11	Considering an ion exchange reaction with protons where CM _{0.5} complexes are formed		
<i>Figure 6.3-12</i>	Considering an ion exchange reaction with protons where C_2M complexes are formed		
<i>Figure 6.3-13</i>	With two types of binding on either site: overall there could be either only adsorption or only ion exchange – or a combination of the two. The functional groups could be e.g. carboxyl and sulfate		
<i>Figure 6.3-14</i>	A two-site model considering pH (protons) and a divalent metal (modified 2:1 stoichiometry). The amounts of bound protons as well as of deposited metal can be calculated. Note the units. Further development of the model is possible and it is outlined in the next section		
<i>Figure 6.3-15</i>	Example of an iterative calculation algorithm for a Donnan-based sorption model. An explicit isotherm relationship of the type $q \sim f(C_f)$ is preferable for practical use and iterations can be eliminated		
<i>Figure 6.3-16</i> <i>Figure 6.3-17</i>	Algorithm of solving model equations without iteration Modeling work has been quite successful and continues		
0			
Table 6	5.1-1 (repeated from Section 6.1) Some sorption isotherm relationships		

6.4 - EQUILIBRIUM MODEL WITH SOLUTION CHEMISTRY

Figure 6.4-1	Speciation of hydrolyzed ionic uranium :	
0	Top mesh: UO_2^{2+} ;	Middle mesh: $(UO_2^{2^+})_2(OH)_2^{2^+}$; Bottom mesh: $(UO_2^{2^+})(OH)^+$;
	(repeated Figure 5-19)	Uranium assumes several ionic forms in solution

- Figure 6.4-3(repeated Figure 5-19)Oralitinassumes several folic forms in solutionFigure 6.4-3(repeated Figure 5-19)Molecular detail of the "egg-box" structure with with
calcium crosslinking two guluronic acid regions in alginate strands. Oxygen atoms
involved in chelation are marked by red dots.Figure 6.4-4(repeated Figure 5-18)Metallic cations can crosslink and gel alginic acid. The
"egg-box" type of linking is mainly in the region of guluronic acid blocks of the
alginic acid molecule

<i>Figure 6.4-1</i> (<i>repeated</i>) Speciation of hydrolyzed ionic uranium : Top mesh: $UO_2^{2^+}$; Middle mesh: $(UO_2^{2^+})_2(OH)_2^{2^+}$; Bottom mesh: $(UO_2^{2^+})(OH)^+$;	
Figure 6.4-5 Com	parison of experimental uranium isotherms and HIEM calculations at different ution pH levels
	ium sorption isotherm surface. Solution pH 2.5 – 4.0, U concentration 0.0 – 6.0 nol/L. (*) Experimental data points; (mesh) HIEM model
	ence of pH on uranium sorption at fixed uranium equilibrium concentrations.
) $U_f = 6.0 \text{ (mmol/g)}; (\blacktriangle) U_f = 4.0 \text{ (mmol/g)}; (\blacklozenge) U_f = 2.0 \text{ (mmol/g)};) U_f = 0.5 \text{ (mmol/g)};)$
Table 6.4-1	Calculation results from equation (6.4-27) and equation (6.4-28), pH 4.0
Table 6.4-2	Calculation results from equation (6.4-27) and equation (6.4-28), pH 2.8
<i>Table 6.4-3</i>	Comparison of [X] calculated with real and approximate $\gamma_t ~~(\text{pH 2.5})$
Table 6.4-4	Comparison of [X] calculated with real and approximate γ_t (pH 4.0)
Table 6.4-5	HIEM model parameters (for uranium)

6.5 - BIOSORPTION BATCH DYNAMICS

Figure 6.5-1	The sorption batch takes time to come to the equilibrium. Since the sorption reactions are inherently fast, it is mainly the mass transfer limitation that we observe
Figure 6.5-2	End-point titration of the uranium batch sorption system (pH 4.0)
Figure 6.5-3	End-point titration of the Cd batch sorption system (pH 4.0).
Figure 6.5-4	There is a relatively small influence of agitation speed on uranium biosorption dynamics
Figure 6.5-5	There is a relatively small influence of agitation speed on cadmium biosorption dynamics
Figure 6.5-6	Influence of biomass particle size on uranium biosorption rate
Figure 6.5-7	Influence of biomass particle size on cadmium biosorption rate
Figure 6.5-8	Influence of formaldehyde cross-linking on cadmium biosorption rate
Figure 6.5-9	Cd biosorption rate and proton release rate at pH 4.0.
	(A): Two stages of cadmium biosorption rate
<i>Figure 6.5-10</i>	Modelling uranium concentration-time profiles at different solution pH values
Figure 6.5-11	Modelling cadmium concentration-time profiles at different solution pH values
Figure 6.5-12	Numerical simulated end-point titration volume profile
Figure 6.5-13	Desorption rate of cadmium from metal-laden Sargassum biomass
Table 6.	5-1 The regressed diffusion coefficients D_e (cm ² /sec)

7 – SORPTION PROCESS PRINCIPLES

Figure 7-1	Concentration gradient is the driving force for sorption and also biosorption
Figure 7-2	For process applications an optimum balance is sought between Δp and particle mass transfer
Figure 7-3	The fixed-bed sorption column system alternates columns for continuous flow operation.
Figure 7-4	Fluidized-bed biosorption system is not the best utilization of the reactor volume
Figure 7-5	The reactor/contactor performance is usually judged at a steady state. Perfect mixing (homogeneous contents) is considered.
Figure 7-6	With an infinite number of mixed stages the system only theoretically approaches the fixed-bed sorption column performance
Figure 7-7	Countercurrent operation requires a solid-liquid separation (usually seives or settling) between stages to isolate coarsely granulated sorbent
Figure 7-8	All three phenomena act in time and space
Figure 7-9	As a result of the three sorption phenomena a dynamic transfer zone develops in the continuous-flow fixed-bed sorption column

The column is gradually saturating at the $C_i = C_f$ The transfer (partial saturation) zone moves through the column as it is getting exhausted.
Column Breakthrough Point and Service Time
A steeper (sharper) breakthrough curve means better utilization of the sorbent in the column
The equilibrium ion-exchange behavior, as characterized by the isotherm, is eventually reflected in the column sorption performance
The "sharpening zone" is shortening as it proceeds slowly in time through the column
The "broadening zone" is expanding in length as it proceeds slowly in time through the column
This summarizes graphically the behavior of the 2 types of transfer zones: the <i>sharp</i> zone is gradually shrinking, while the <i>broad</i> zone is expanding as they proceed slowly in time through the sorption column
 Other sorbates in the system may cause "A": 1) to leave the column faster with an early breakthrough as compared to its pure system; 2) to "overshoot" as its exit concentration exceeds its feed concentration
The column exit concentration overshoot behavior in a mixed-sorbate system: The sorbate with the lowest affinity for the given sorbent exits first and overshoots most
Dynamic sorption behavior reflects the complex regime in the sorption column. This makes the optimal column design quite a challenge.
Example of a hypothetical biosorption effluent treatment plant design specifications
Schematic flowchart of a biosorption plant for treating electroplating wastewater
Example of a possible full-scale biosorption plant installation

8 – COLUMN PERFORMANCE MODELING

Figure 8.1-1	What used to be called a "theoretical approach" can nowadays go a long way and it is essential for optimal process design and operation
<i>Figure 8.1-2</i>	Apart from intra-particle mass transfer, fluid flow properties represent the most significant factor affecting the performance of a sorption column
Figure 8.1-3	Powerful computer-based numerical methods are now easily available for solving the model equations
Figure 8.1-4	Some basic models used for estimating the sorption column performance. Several will be discussed in more detail in this Chapter
Figure 8.1-5	Experimental points and breakthrough curves generated by <i>IMPACT</i> simulation program for a column with Sargassum fed with an equimolar 3-metal mixture [7]
Figure 8.2-1	While the ECM neglects all the mass transfer, eventually affecting the breakthrough curve shape, it is useful for multi-component mixtures: predicting the sorbate outlet sequences and concentration overshoots as well as the sorption column service time.
<i>Figure 8.2-2</i>	Plateaus and Transitions considered in the column for the purpose of the ECM calculations
Figure 8.2-3	Proportionate-pattern or gradual transition developing in the sorption column with time
Figure 8.2-4	Constant-pattern or abrupt transition developing in the sorption column with time (EC Model)

Figure 8.2-5	The ECM plot layout
Figure 8.2-6	Algorithm for computer solution of equations (8.2-4,9,10)
Figure 8.2-7	Example of Plateaus and Transitions in the ECM plot for column performance evaluation
Figure 8.2-8	A typical column effluent concentration overshoot caused by competitive ion exchange
<i>Figure 8.2-9:</i>	 A: component with a (+) slope transition; C: component with a (-) slope transition
Figure 8.2-10a	Compounds A and C on B-form biosorbent
Figure 8.2-10b	Compounds A and B on C-form biosorbent
Figure 8.2-10c	Compounds B and C on A-form biosorbent
Figure 8.1-11a	Affinity of Fe <cu !<="" and="" breaks="" concentration="" cu="" earlier="" fe="" fe:="" higher="" is="" much="" of="" overshoots="" td="" than="" that="" the="" through=""></cu>
<i>Figure 8.2-11b</i>	Affinity of Zn <cu and="" concentration="" cu="" earlier!<="" higher="" is="" much="" of="" overshoots="" td="" than="" that="" the="" zn="" zn:=""></cu>
<i>Figure 8.2-11c</i>	Affinity of Cd <cu !<="" and="" cd="" concentration="" cu:="" earlier="" is="" lower="" much="" of="" overshoots="" td="" than="" that=""></cu>
Figure 8.2-11d	Affinity of Zn <cu, !<="" and="" cd="" concentration="" higher="" is="" much="" no="" of="" overshoot="" td="" than="" that="" the="" zn:=""></cu,>
<i>Figure 8.2-12</i>	Analysis of concentration overshoots for columns packed with B-sorbent fed with A and C (A=Cu; C=Ca).
Figure 8.2-13a	A sorption column effluent concentration history predicted by the ECM
Figure 8.2-13b	Experimental effluent concentration history. A Ca-biomass column treating a (Cu+Cd+Zn) metal mixture
<i>Figure 8.2-14</i>	Comparison of Zn breakthrough from 4-component and 2-component sorption systems
Table 8.2-1Ion Exchange Equilibrium Constatnts for Metals with Sargassum BiomassTable 8.2-2Evaluating a biosorption process to treat heavy metal pollution	
Figure 8.3-1	The powerful MTM requires the knowledge or estimate of the sorbate diffusion coefficient(s) and the equilibrium reaction parameters.
Figure 8.3-2	Coefficient(5) and the equilibrium reaction parameters.
Figure 8.3-3	Dimensionless ion exchange isotherm diagram
1 151110 010 0	
•	Dimensionless ion exchange isotherm diagram
Figure 8.3-4	Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature)
Figure 8.3-4 Figure 8.3-5	Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature) The dimensionless groups used in the MTM Prediction of the Ca-biomass sorption column service time by the MTModel. Done
Figure 8.3-4 Figure 8.3-5 Figure 8.3-6	 Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature) The dimensionless groups used in the MTM Prediction of the Ca-biomass sorption column service time by the MTModel. Done for the Zn breakthrough in a (Cu+Cd+Zn) system Theoretically, N different mass transfer coefficients and 3(N-1) equations are
Figure 8.3-4 Figure 8.3-5 Figure 8.3-6 Figure 8.3-7	 Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature) The dimensionless groups used in the MTM Prediction of the Ca-biomass sorption column service time by the MTModel. Done for the Zn breakthrough in a (Cu+Cd+Zn) system Theoretically, N different mass transfer coefficients and 3(N-1) equations are necessary when N sorbates are considered The ECM procedure can assist in simplifying a multisorbate sytem into a binary
Figure 8.3-4 Figure 8.3-5 Figure 8.3-6 Figure 8.3-7 <mark>Figure 8.4-1</mark>	 Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature) The dimensionless groups used in the MTM Prediction of the Ca-biomass sorption column service time by the MTModel. Done for the Zn breakthrough in a (Cu+Cd+Zn) system Theoretically, N different mass transfer coefficients and 3(N-1) equations are necessary when N sorbates are considered The ECM procedure can assist in simplifying a multisorbate sytem into a binary system that can be handled by the MTM Response of the uranium column outlet concentration to the step function in the column inlet (switch to distilled water).
Figure 8.3-4 Figure 8.3-5 Figure 8.3-6 Figure 8.3-7 Figure 8.4-1 Figure 8.4-2 Figure 8.4-3	 Dimensionless ion exchange isotherm diagram Suitable equilibrium models need to be established (Chapter 6 or from the literature) The dimensionless groups used in the MTM Prediction of the Ca-biomass sorption column service time by the MTModel. Done for the Zn breakthrough in a (Cu+Cd+Zn) system Theoretically, N different mass transfer coefficients and 3(N-1) equations are necessary when N sorbates are considered The ECM procedure can assist in simplifying a multisorbate sytem into a binary system that can be handled by the MTM Response of the uranium column outlet concentration to the step function in the column inlet (switch to distilled water). (F = 175 ml/h, V_{bed}=280 ml, biosorbent = 22.64 g) Comparison of experimental uranium and Mass Transfer Model calculated

9 - BIOSORBENT MATERIAL PREPARATION

Figure 9-1	Granulation of the biosorbent is essential for its effective application in a sorption process
Figure 9-2	Cheap biomass raw material comes from two major sources: as industry waste or an ocean-based natural and renewable resource
Figure 9-3	Seaweeds represent plentiful and renewable biomass that could be collected and/or propagated
Figure 9-4	Formulating a sorbent means striking a balance between the "micro" and "macro" considerations
Figure 9-5	A sorbent particle has to be sturdy, rigid and easily penetrable by the sorbate compound
Figure 9-6	We want to quantify and to be able to also manipulate the sorption particle properties
Figure 9-7	Formulated and processed granules need to be tested and characterized
Figure 9-8	Formulating a sorbent means striking a balance between the "micro" and "macro" considerations
Figure 9-9	A number of types of chemical treatment aims at improving different aspects of biosorbents
Figure 9-10	Active biosorbent material is "embedded" in a permeable substance making up the particle
Figure 9-11	Permeability and durability of the encapsulating membrane may be a problem
Figure 9-12	Both procedures reinforce the particle but may result in diminished sorption performance
Figure 9-13	There are many crosslinking procedures – they invariably represent chemical interferences in the particle that must already be in existence
Figure 9-14	FA crosslinking takes place in 2 stages
Figure 9-15	UFA crosslinking with DMU does a different job and yields byproducts
Figure 9-16	A generalized schematic flowchart of biomass processing into sorbent granules
Figure 9-17	When biosorbent undergoes chemical treatment there are always chances that its performance may suffer
Figure 9-18	Fluidization and agglomeration is involved in both granule-making processes that are highly empirical
Figure 9-19	The sorption column breakthrough curve AND the pressure drop are the most important continuous-flow sorption process characteristics and operating parameters
Figure 9-20	The optimum compromise has to be sought between the column mass transfer performance and its operating pressure drop
Figure 9-21	Ideally, NO granulation would need to be done. Sargassum biosorbent has been such a case
Figure 9-22	Performance of every sorption process depends directly on the preparation of the sorbent
Figure 9-23	Formulation of biosorbent materials for application has to be carefully considered, optimized and the sorption performance examined after each treatment or procedure
Figure 9-24	Opposite to the uptake (sorption), DESORPTION is an important study area leading to regeneration of the sorbent and to the eventual recovery of sorbate
Figure 9-25	In equilibrium batch desorption studies, residual uptake of the sorbate (here at low pH) could distort the desorption results and conclusions
Figure 9-26	A high-concentration peak of uranium exited the experimental column upon low-pH (pH 1.2) desorption wash
Figure 9-27	Single-component desorption: YELLOW: High and narrow elution peak is desirable for desorption particularly when the eluate is to be further processed (recovery !). BLUE: Low, flat and trailing elution peak is a sign of desorption problems

- Figure 9-28 Multi-component operation: YELLOW: Low-affinity compound A breaks through first as it is replaced in the column by B and C.
 GREEN: Middle-affinity compound B also overshoots but less upon later
 - breakthrough. BLUE: High-affinity compound **C** eventually leaves the column in the normal
 - breakthrough
- *Figure 9-29* (repeated *Figure 2-21*) Concentration of the sorbate in the effluent eluate is important for its further recovery (or disposal)
- *Figure 9-30* (repeated *Figure 2-22*) Biosorbent Solids to eluting Liquid ratio (S/L) is of importance to overall process effectiveness

Figure 9-31 (repeated *Figure 2-23*) Complete sorbent regeneration may take two or more operations, usually "in situ" in the column

- Table 9-1 [9]
 Characteristics of pre-treated Sargassum biomass
- Table 9-2 [9] Behavior of modified Sargassum biomass during Zn biosorption
- *Table 9-3* [9] Multicomponent Langmuir model parameters:
 - Equilibrium constants K (L/meq), K_{Zn}/K_M ratios and error function F_M
- Table 9-4 [9]Multicomponent Langmuir model parameters:
Equilibrium constants K (L/meq), K_M/K_K ratios

10 – MONOCLONAL ANTIBODIES BIOSORPTION

Figure 10-1	Example of a different type of biosorption: using monoclonal antibodies for bio- product recovery
Figure 10-2	Highly selective and immobilized sorbent (mAb) retains only the desired type of sorbate (white) from a mixture of other molecules
Figure 10-3	Antibodies are glycopeptides, this one is "IgG1"
Figure 10-4	Chromatography is an operation based on a semi-continuous-flow sorption process
Figure 10-5	Working with antibodies again represents a multi-faceted and interdisciplinary task
Figure 10-6	Antibodies can be produced either <i>in vivo</i> , or <i>in vitro</i> by a laboratory technological process
Figure 10-7	Techniques of eluting a loaded column can facilitate a difficult separation
Figure 10-8	Affinity Chromatography – for purification of antibodies using immobilized protein (UPPER), or (LOWER) using immobilized antibodies to 'immunosorb' a protein
Figure 10-9	Small columns used in laboratory immuno-affinity chromatography. Larger-scale operation is still in the future
Table 1	<i>0-1</i> Comparative mAb production scale
Table 1	<i>0-2</i> Commonly used affinity fusion systems
Table 1	<i>0-3</i> Summary of the mAbs work cited