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Detoxification of metal-bearing effluents: biosorption for the next century

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Abstract

Metals can be removed and concentrated from solutions by using biomass material. Conservative estimates give new biosorbents the potential share amounting to US$27 million/year of the currently existing environmental market in North America alone. Very high cost-effectiveness of biosorption technology would tend to open new opportunities currently untapped. Biosorbents can be regenerated for multiple reuse, offering the metal recovery possibility from concentrated wash solutions. Relatively simple metal biosorption processes can meet the progressively stricter environmental discharge criteria. As with any up-start technology, the continuing R&D is crucial. The interdisciplinary nature on both sides, application as well as R&D, poses quite a challenge. While there are numerous potential industrial clients, a successful biosorption enterprise will have to have courage, multidisciplinary skills and adequate financing.

Keywords: Metal; Effluent; Biosorption

1. Metals: environmental threat

By far the greatest demand for metal sequestration comes from the need of immobilizing the metals 'mobilized' by and partially lost through growing and ever-intensifying human technological activities. It has been established beyond any doubt that dissolved particularly heavy metals escaping into the environment pose a serious health hazard. The threatening presence of heavy metals has even been linked to the demise of the Roman empire in the past [1]. Nowadays, with the exponentially increasing population the need for controling heavy metal emissions into the environment is even more pronounced. This is best done right at the source of such emissions, before toxic metals enter the complex ecosystem. To follow the fate of metallic species after they enter the ecosystem becomes very difficult and they start to inflict the damages as they move through from one ecological trophic layer into another. They accumulate in living tissues throughout the food chain which has humans at its top (Fig. 1). The danger multiplies and humans eventually tend to receive the problems associated with the toxicity of heavy metals pre-concentrated and from many different directions. The resulting health problems demonstrate themselves on the acute as well as chronic levels and are reflected in the well-being of individuals and in society's spiraling health care costs. Con-

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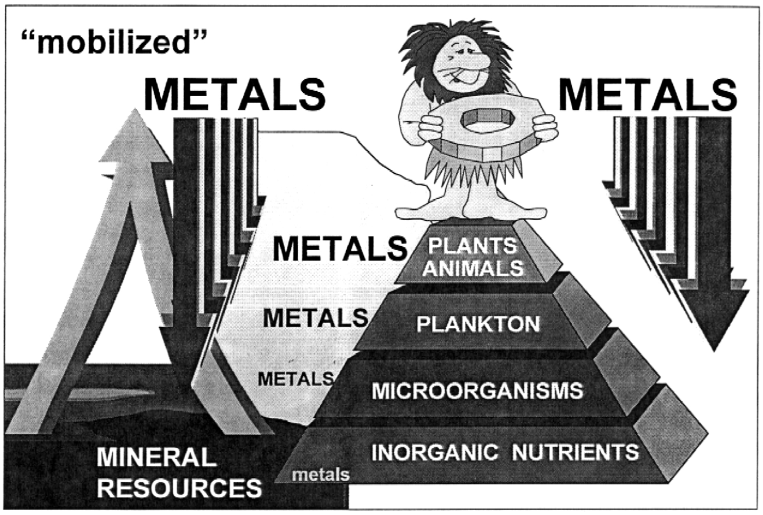

Fig. 1. With increasing amounts of metals "unearthed", amounts of toxic heavy metals entering the environment increases. They threaten humans as they become pre-concentrated throughout the food chain.

trolling heavy metal discharges and removing toxic heavy metals from aqueous solutions has become a challenge for the 21st century.

1.1. Environmental pressures

• Under the public and media pressure, governments introduce and progressively enforce stricter regulations with regard to the metal discharges particularly for industrial operations.

• The compounding toxic effects of heavy metals in the environment are being recognized and their dangerous impacts better understood.

• The currently practiced technologies for removal of heavy metals from industrial effluents appear to be inadequate, creating often secondary problems with metal-bearing sludges which are extremely difficult to dispose of. Due to their classification as "toxic substances" they require special handling, disposal methods and sites. Their handling and disposal is, in most instances, closely monitored by the governments.

• The currently available "best treatment technologies" for metal-bearing effluents are either not effective enough or are prohibitively expensive and inadequate considering the vast wastewater quantities.

1.2. Conventional metal-removal technologies

Municipal sewage treatment plants are not designed and equipped for handling toxic wastes. Metals and their toxicity persist even in the sludges and by-product streams of municipal sewage treatment plants. Heavy metals need to best be removed at the source in a specially designed 'pre-treatment' step. This specific treatment needs to be cheap because it most often deals with large volumes of effluents.

The conventional approaches to heavy metal removal are using technologies listed in Table 1. It is not within the framework of this text to discuss these conventional techniques but it would suffice to say that as the emission standards tighten they are becoming progressively more inadequate. On the other hand, better technologies are more costly and often just not feasible. The search is on for efficient and particularly cost-effective remedies. Biosorption promises to fulfill the requirements. This novel approach is competitive, effective and cheap.

1.3. Biosorption

Under the term of metal "biosorption" a passive process of metal uptake and sequestering is understood whereby the metal is sequestered by chemical

Table 1
Conventional metal removal technologies

Method	Disadvantages	Advantages
Chemical precipitation and filtration	for higher concentrations	simple
	difficult separation	cheap
	NOT effective	
	resulting sludges	
Chemical oxidation or reduction	chemicals required (not universal)	mineralization
	biological system (slow rates)	mineralization
	climate sensitive	
Electrochemical treatment	for high concentrations	metal recovery
	EXPENSIVE	
Reverse osmosis	high pressures	pure effluent (for recycle)
	membrane scaling	
	EXPENSIVE	
Ion exchange	sensitive to particles	effective
	EXPENSIVE RESINS	pure effluent metal recovery possible
Adsorption	not for metals	conventional
		sorbents (carbon)
Evaporation	energy intensive	pure effluent (for recycle)
	EXPENSIVE	
	resulting sludges	

sites naturally present and functional even when the biomass is dead. The advantage of biosorption is in using biomass raw materials which are either abundant (seaweeds) or wastes from other industrial operations (fermentation wastes). The unique capabilities of certain types of biomass to concentrate and immobilize particularly heavy metals can be more or less selective. That depends, to a certain degree on:

- the type of biomass,
- the mixture in the solution,
- the type of biomass preparation,
- the chemico-physical process environment.

Broad-range biosorbents can collect all the heavy metals from the solution with a small degree of selectivity among them. It is important to note that concentration of a specific metal could be achieved either during the sorption uptake by manipulating the properties of a biosorbent, or upon desorption during the regeneration cycle of the biosorbent.

1.4. Metal removal / recovery priorities

An example of the prioritization for recovery of 10 metals in Table 2 may be perhaps somewhat simplistic. It serves as an example of considerations to take when choosing the metals of interest for either removal and/or recovery. These considerations rank the metals into three general priority categories:

1. environmental risk (ER);
2. reserve depletion rate (RDR);
3. combination of the two above factors.

Table 2
Ranking of metal interest priorities

Relative priority	Environmental risk	Reserve depletion	Combined factors
High	Cd	Cd	Cd
	Pb	Pb	Pb
	Hg	Hg	Hg
	–	Zn	Zn
Medium	–	Al	–
	Cr	–	–
	Co	Co	Co
	Cu	Cu	Cu
	Ni	Ni	Ni
	Zn	–	(see High)
Low	Al	–	Al
	–	Cr	Cr
	Fe	Fe	Fe

Table 3
Major target industrial sectors

Industry	Metals	Possible interferences
Mining operations	Cations: Cu, Zn, Pb, Mn, U, ...	Fe, Al
	Anions: Cr, As, Se, V, ...	sulphates, phosphates
Electroplating operations	Cr, Ni, Cd, Zn	Fe, surfactants
Metal processing	Cu, Zn, Mn,	Fe, Al, surfactants
Coal-fired power generation	Cu, Cd, Mn, Zn, ...	Fe, Al
Nuclear industry	U, Th, Ra, Sr, Eu, Am, ...	Fe
Special operations	Hg, Au and precious metals	

The environmental risk assessment could be based on a number of different factors which could even be weighed. The RDR category is used as an indicator of probable future increase in the market price of the metal. When coupled with the ER in this example there is an indication that Cd, Pb, Hg and Zn are a high priority. However, the technological uses of Hg and Pb may be considered declining, while the Cd use is on the increase. These projections and the degree of risk assessment sophistication could change the priority sequence among the metals considered. The metallic elements handled by the nuclear industry represent a very special category.

Table 3 lists the key industrial sectors that are likely to have metal-bearing effluent discharge problems and deserve an especially close scrutiny. Naturally, they are the most likely potential clients for removal of metals from their wastewaters.

2. Metal biosorption development areas

With new discoveries of highly metal-sorbing biomass types there is a real potential for the introduction of a whole family of new biosorbent products which are likely to be very competitive and cost-efficient in metal sorption. These materials can provide a basis for a whole new technology of metal removal and recovery. The search for cheap biosorbent materials for the purpose focuses on examining the potential of waste and/or abundant biomass types. The discovery of metal biosorption was due to recognizing the fact that metal concentration by biomass was based on its ‘chemical’ properties rather than biological activity. Biosorption research took off in the 1980s.

While there are copious quantities of waste activated sludge from conventional biological wastewater treatment plants all over the world, the metal-sorbing capacities of these sludges representing very mixed and heterogeneous microbial populations are usually rather low. There may be some possibilities for improving their metal-sorbing capacity but the heterogeneity of the biomass makes this difficult and doubtful. Microbial biomass can be grown extremely fast and in many instances there are large quantities of it posing even a serious disposal problem for fermentation industries. These are possibly the cheapest biomass sources. It is necessary to realize that some “waste” biomass is actually a commercial commodity, not a waste: this applies particularly for ubiquitous brewer’s yeasts sold on the open market for a good price usually as animal fodder. A unique and ubiquitous type of macroscopic biomass known for its metal-sorbing potential are seaweeds, marine algae.

For preparation of suitable biosorbent materials from industrial waste biomass for application in large-scale sorbing equipment, the consistency of the biomass will have to be altered. Normally, industrial waste biomass appears as wet ‘mud’ or dry cake or powder. It will have to be processed into durable small granules to withstand the conditions of the sorption process. Seaweed biomass, on the other hand, does have a certain rigid macro-structure of its own and in some instances it has been revealed to offer excellent metal-sorbing properties. At certain ocean locations, seaweeds are plentiful and very fast growing. At some locations, they threaten the tourist industry by spoiling pristine environments and fouling beaches. Turning seaweeds into a resource can be quite beneficial to some local economies. From simple collection of the seaweed biomass the trend points at aquaculture methods as the demand may be increasing.

As a fall-back, high metal-sorbing biomass could even be specifically propagated relatively cheaply in fermentors using low-cost or even waste carbohydrate-containing growth media based on, e.g. molasses or cheese whey.

2.1. Screening

Screening of microbial biomass types for metal biosorption constitutes an important, albeit tedious, way of identifying the most promising types of biomass. In the absence of deeper knowledge with regard to metal biosorption, various materials have to be tested to assess their metal-sorbing potential. This is done mainly based on simple batch equilibrium sorption tests. For the sake of expediency at this stage of work many errors have been committed and even reported in the literature by those who do not quite understand equilibrium sorption concepts. The most appropriate method of assessing the biosorbent capacity is the derivation of a whole sorption isotherm [2]. Anything else represents a potentially misleading shortcut, which may lead to outright erroneous conclusions. A very comprehensive list of metal biosorption test results was assembled in 1995 [3].

2.2. Biosorption uptake studies

Equilibrium sorption studies with simple one-metal sorption systems are usually completed first and gradually expanded into examining multimetal biosorbent behavior in conjunction with the selected biosorbent. Then good experimental planning is essential and result interpretation becomes more involved. Kinetics studies yield more accurate information on sorbent uptake rates which are known to be inherently very fast for sorption reactions and difficult to follow. Rapid sorption reactions are usually NOT the rate controlling factor in the (bio)sorption process. It has been widely recognized and confirmed that it is actually the intraparticle mass transfer rate which represents the bottleneck and is thus controlling the rate of the entire sorption process. The particle size and its structure(s) are thus very important.

In the ‘real world’ the solutions processed are rarely pure. The assessment of the effect on the biosorption performance of ‘impurities’ that may be present is of interest. These could be both organic and inorganic, dissolved, colloidal or suspended. Actually, different metal ions could interfere with the sorption process, as might other ionic species. The choice of those to be studied has to be made judiciously and with regard to the real process conditions. At this point, asking a pragmatic question “what is it all good for?” may be very helpful in terms of guiding the choices of factors to be studied and which may eventually be important in the overall mission of the process itself.

The same applies to the choice of environmental factors to be examined some of which tend to influence the sorption process more than others. However, the solution pH and ionic strength are usually the most obvious and important ones to look at. A great deal of information can be derived from the equilibrium sorption studies that provide the information basis for the design of the biosorption process.

Dynamic sorption studies are invariably more demanding. They involve liquid flow and relatively complex mass transfer and reflect more closely the actual configuration of the sorption process. Correct and non-trivial interpretation of experimental results is important and becomes technically and scientifically rather sophisticated [4,5]. Particularly considering the contemporary state of the art in sorption processes, advanced sophistication in dynamic sorption studies is expected. It is obvious that simplistic observations of experimental “break-through” curves (Fig. 2) resulting from the conventional operation of a flow-through sorption column will not suffice. These types of results are usually very specific and cannot be used for explaining the behavior of another, even similar, sorption system.

The difficulty of analyzing the dynamic sorption behavior stems from the fact that such systems involve the sorption equilibrium behavior, mass transfer, and fluid flow properties all at the same time as the saturation of the sorbent progresses not only in time but also in space of the sorption column. In the sorption column contactor, the steady state zone is

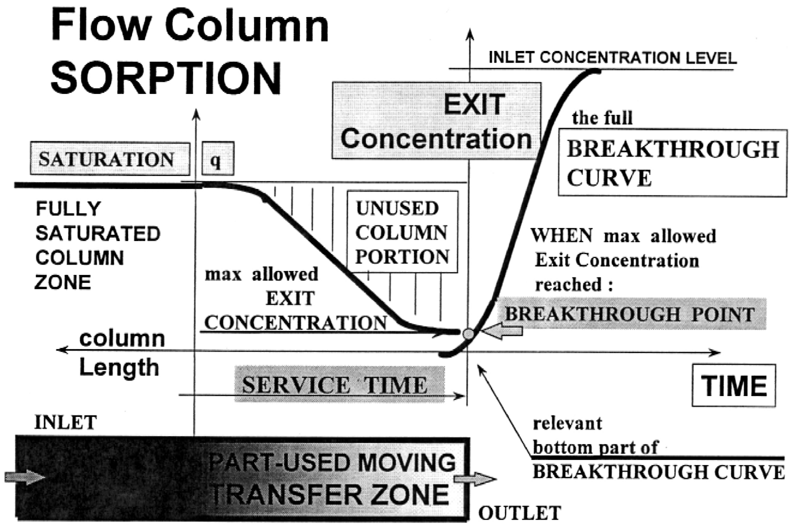

Fig. 2. When the sorption column becomes saturated, it ceases to function and the metal "breaks through". This situation determines the useful service time of the column. The size of the still unsaturated column portion at this time determines the degree of column utilization.

moving right along the column length pushing the transitional sorption zone ahead of itself. In multi-metal sorption systems, where ions of different metals feature different affinities toward the sorbent the whole system becomes even more complex as chromatographic effects due to simultaneous displacement of ions already deposited take place.

When compared to the sorption fixed-bed column reactor, the continuous-flow stirred-tank reactor (CSTR) lies on the opposite end of the reactor spectrum. While the flow in the theoretical fixed-bed reactor is considered as non-mixed plug flow, the basic assumption for the CSTR is complete and instantaneous mixing. Its contents is thus considered homogeneous. Its outflow reflects exactly what is inside. This means that only a very small concentration difference as a driving force may be thus available for the sorption process in the CSTR. Normally, the CSTR would not be the reactor of choice for a sorption process unless it is organized as a series of mixed reactors. Technological process requirements may warrant such an operational mode in some cases such as sorption from particle-containing solutions (suspensions) which cannot be done in a packed-bed column without it becoming rapidly plugged up. To fluidize the bed in the column may prevent the plugging (Fig. 3). Performance estimation of such hybrid systems becomes especially challenging particularly considering their complex fluid dynamics.

2.3. Desorption

If the biosorption process were to be used as an alternative in the wastewater treatment scheme, the regeneration of the biosorbent may be crucially important for keeping the process costs down and to opening the possibility of recovering the metal(s) extracted from the liquid phase. For this purpose it is desirable to desorb the sorbed metals and to regenerate the biosorbent material for another cycle of application. The desorption side of the process should:

- yield the metals in a concentrated form;
- restore the biosorbent to close to the original condition for effective reuse with:
  - undiminished metal uptake;
  - no physical changes or damage.

Extensive 'desorption' work may be necessary for assessing whether this is possible and under what conditions. The desorption and sorbent regeneration

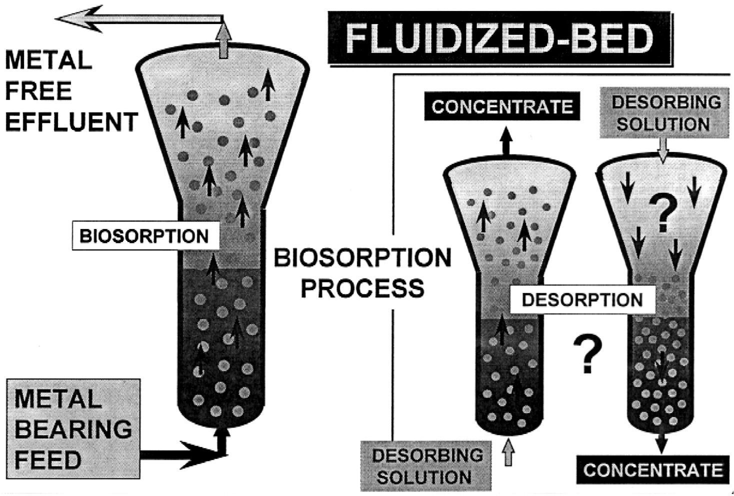

Fig. 3. The fluidized-bed sorption contactor would feature lower sorption efficiencies. However, it allows for some suspended solids in the feed stream. The usually practised in-situ regeneration is not quite straightforward for such a system.

studies might require somewhat different methodologies particularly for fluidized-bed arrangements (Fig. 3). While the regeneration of the biosorbent may be accomplished by washing the metal-laden one with an appropriate solution, the type and strength of this solution would depend on just how the deposited metal has been bound. Screening for the most effective regenerating solution is the beginning [6]. In batch tests of desorbing solutions, one has to realize that the desorbed sorbate (metal) stays in the solution and a new equilibrium is established between that and the one (remaining) still fixed on the biosorbent. This leads to the concept of a "desorption isotherm" where the equilibrium is strongly shifted towards the sorbate dissolved in the solution [7]. However, some residual sorbate may still be retained by the biosorbent to a various degree. The effect of the desorption wash on the structure of the biosorbent has to be established (microscopy, structure tests, pressure drop, etc.).

Due to different affinities of metal ions for the predominant sorption site (under the solution conditions), there will be a certain degree of metal selectivity by the biosorbent on the uptake. Similarly, another selectivity may be achieved upon the elution–desorption operation [8,9]. Advantage could be taken of this selectivity on the desorption side of the operation which can contribute to the separation of metals from one another if desirable.

"The proof of the pudding", so to speak, for the sorption process is its overall capacity to concentrate the sorbate metal. This is assessed by expressing a simple overall process parameter, the Concentration Ratio (CR). Obviously, the higher the CR, the better is the overall performance of the sorption process making the eventual recovery of the metal more feasible as it becomes concentrated in the small volume of the elutant solution. Following desorption of the metal(s), the column may still be pre-treated by another type of wash solution in order to achieve its optimum performance in the subsequent metal uptake cycle. The types of this treatment may vary.

The potential recovery of the metal from concentrated desorption solutions is another question. It would usually be carried out as an independent metal recovery operation, in a different plant, by an entirely different process or a sequence of operations. It is most often feasible to use electrowinning procedures to recover metals from concentrated solutions.

2.4. Mechanism of metal biosorption

Adsorption and desorption studies invariably yield some information on the mechanism of metal biosorption: how is the metal bound within the biosorbent. This knowledge is essential for understanding of the biosorption process and it serves as a basis for quantitative stoichiometric considerations which constitute the foundation for mathematical modeling of the process [4,10–12].

A number of different metal-binding mechanisms has been postulated to be active in biosorption metal uptake such as:

- chemisorption by ion exchange, complexation, coordination, chelation;
- physical adsorption and microprecipitation.

There are also possible oxidation/reduction reactions taking place in the biosorbent [13]. Due to the complexity of biomaterials used it is quite possible that at least some of these mechanisms are acting simultaneously to varying degrees depending on the biosorbent and the solution environment. More recent studies with fungal biomass and seaweed in particular have indicated a dominant role of ion exchange metal binding [14–17]. Indeed, the biomass materials offer numerous molecular groups that are known to offer ion exchange sites, carboxyl, sulfate, phosphate, and amine, could be the main ones.

When the metal–biomass interaction mechanisms are reasonably understood, the work can begin on optimizing the biosorption process on the molecular level. That could include even manipulation of selectivity for particular metal(s) of interest. An intriguiging long-range challenge would be to manipulate the metal biosorption properties of the biomass already when it is being biosynthesized during the growth of the cell [18].

The knowledge of metal biosorption mechanisms could lead to developing economically attractive analogous sorbent materials [19,20]. Better understanding of the metal biosorption phenomenon would simplify the screening process which could be much more focused. The possibility of 'activating' those biomaterials that do not exhibit apparent biosorbent behavior is also very attractive. Simple and economically feasible pretreatment procedures for suitable biomaterials may be devised based on better understanding of the metal biosorbent mechanism(s).

2.5. Modeling

Mathematical modeling and computer simulation of biosorption offers an extremely powerful tool for a number of tasks on different levels. It is essential for process design and optimization where the equilibrium and dynamic test information comes together representing a multivariable system which cannot be effectively handled without appropriate modeling and computer-based techniques. The dynamic nature of sorption process applications (columns, flow-through contactors) makes this approach mandatory. When reaction kinetics is combined with mass transfer which is in turn dependent on the particle and fluid flow properties only a reasonably sophisticated apparatus can make sense out of the web of variables [10,12,15]. The know-how needs to be transferred from established areas of sorption processes as developed for activated carbon or ion exchange resins.

Biosorption process modeling is particularly useful for *predicting* the process performance under different conditions. Computer simulations can then replace numerous tedious and expensive experiments to the extent that only the key experiments can be selected and need to be carried out to verify the predictions. Needless to say, the simulations are only as good as the model behind them is. However, advanced sophistication in this area and availability of very powerful computer hardware and software makes contribution of the process modeling/simulation activity very realistic and indispensable indeed.

Biosorption process modeling then can:

- guide experimental research;
- optimize a given process;
- provide basis for process control strategies;
- provide a process diagnostic tool.

A whole new area is opening up in modeling of molecules, their parts and interactions. "Seeing" how the biosorbent works on a molecular level would aim at purposefully preparing, 'engineering', a 'better biosorbent'. While significant inroads have been made in revealing protein and nucleic acid structures and their behavior, carbohydrate chemistry which seems to be at the basis of the biosorption behavior still has not significantly benefited from these advanced computer modeling techniques. The opportunity beckons.

2.6. Granulation

The last but not the least area to be developed in the field of biosorption is the granulation of biosorbent materials. It is not necessarily a scientifically glamorous endeavour since it appears to be rather empirically based but without it reliably delivering *granulated* biosorbents there may not be any scaled-up biosorption applications. The most effective mode of a sorption process is undoubtedly based on a fixed-bed reactor/contactor configuration. The sorption bed has to be porous to allow the liquid to flow through with minimum resistance but allowing the maximum mass transfer into the particles. The particles thus should be as small as practical for the reasonable pressure drop across the bed. This concept of this type of a process compromise is schematically depicted in Fig. 4. Ion exchange resins manufactured for the same purpose generally feature particle sizes between 0.7 and 1.5 mm. Biosorbents should come in about the same size. Hard enough to withstand the application pressures, porous and/or 'transparent' to metal ion sorbate species, featuring high and fast sorption uptake even after repeated regeneration cycles. Considering the vast variety of and differences in the raw biomass materials, this is a tall order.

However, conventional granulation technologies are rather advanced and the chances are very good that some applications will yield desirable biosorbent granules [21–23]. At the same time, the broad variety of biomass types will undoubtedly require extensive experimentation for this purpose. There may be also formidable 'logistical' problems because of transportation of raw biomass. Microbial biomass comes with a high water content and is prone to decay. Its drying may be required if it cannot be processed directly on location in the wet state. However, bulk processing may not add significantly to the costs. Similarly with the seaweed biomass—following the collection, it would have to be processed on location immediately in the wet state or at least sun dried. The actual granulation procedures could differ substantially depending on whether dry or wet biomass is to be processed.

In order to make biosorbent granules, the high-sorbing biomass needs to be "immobilized", made into suitable solid particles by a using technique such as:

- *entrapment* in a strong but permeable matrix;
- *encapsulation* within a membrane-like structure.
- *bonding* of smaller (microscopic) particles.

Each of these techniques has certain advantages and disadvantages, some of which are indicated in Table 4.

Most of the methodologies used for particle making (granulation) have been reasonably well devel-

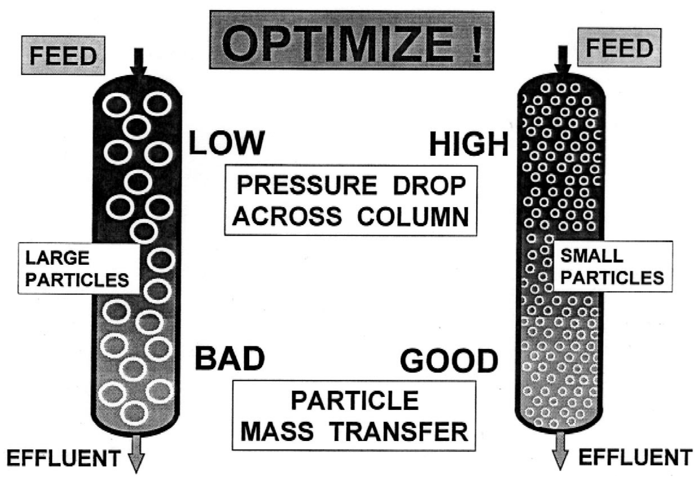

Fig. 4. The best sorption performance would be for small particles with minimized intra-particle mass transfer. The pumping pressure has to be high to push the liquid through a small-particle bed. A feasible operation compromise has to be devised.

Table 4
Biomass immobilizaton

Immobilization	Advantages	Disadvantages	References
Gel entrapment	known cheap	limitations:	[27]
		mass transfer	[28]
		catalyst densities	[29]
Encapsulation	higher catayst densities	fragile capsules	[30]
		mass transfer barrier	[31]
Biomass cross-linking	increased strength	loss of activity not universal	[32]
No treatment	cheap	irregularities	[24] [33]

oped for many different types of materials. However, the special nature and widely varied chemistry associated with different biomass types requires special efforts and continuing investigations in order to obtain the desired granule properties.

While granulation is essential for advancement of biosorption as a technology, it is more of a trial-and-error task making it difficult for academic researchers to make a significant contribution. Somewhat distant from the "research" part of the typical R&D effort it seems to be more of a product "development" type activity with inherent logistical hurdles involved.

2.7. Biosorption process operation

The most effective configuration of the biosorption process, as the case is for most sorption processes in general, is the flow-through packed bed sorption column (Fig. 2). Its performance is crucially dependent on the quality of the sorption particles it is filled with. Multiple reuse of the active sorbent particles greatly increases the process economy. The column operation would often consist of two or three cycles (Fig. 5): the sorption uptake period followed by desorption of the deposited species and sometimes regeneration of the column for the next uptake cycle is necessary [9,24,25].

In general, the biosorption process feasibility depends primarily on the sorption material uptake. The overall process performance, in correspondence to the column operating cycles, is affected by the efficiency of the desorption and regeneration cycles. While the biosorption process feasibility rests on the availabilities and costs of the biomass raw material, the way this raw material is formulated into an active biosorbent is very important. That refers to its granulation and pre-treatment processing which determines the price of the final product [26].

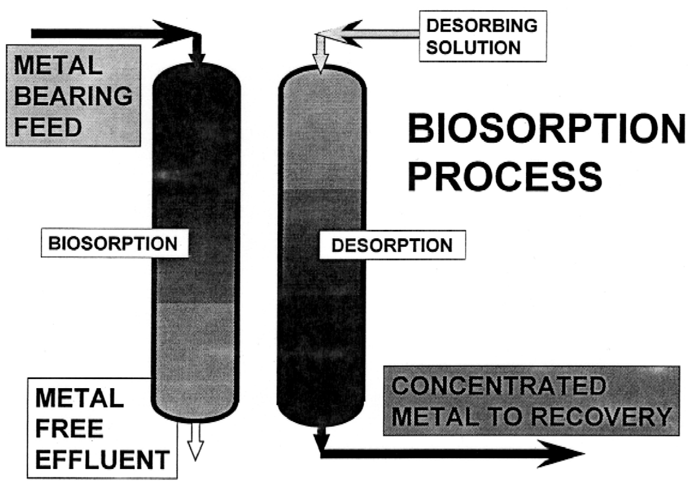

Fig. 5. The sorption column overall operation cycle consists of the sorption and desorption periods. The number of cycles a column can go through depends on many factors.

2.8. Project disciplines

It is obvious that many different and challenging contributions can be made on the path to developing biosorption from a scientific curiosity to useful applications. There is no doubt that there is a potential in this field. Apart from individual scientific challenges, there is a special one in crossing the boundaries of conventional science disciplines to accomplish the goal: to develop understanding of the (metal) biosorption phenomenon that could reliably serve as a base for a successful technological enterprise.

Different science disciplines can make the best contribution at different points of the field as they were discussed above. While a great deal of overlap exists in those crucial areas, no one discipline could do it all. The challenge is in developing the individual projects undertaken on an interdisciplinary basis and in coordinating the efforts of professionals with different science backgrounds needed.

The two types of backgrounds which might undoubtedly contribute most in developing the science basis of biosorption in the direction of its applications are chemistry, including biochemistry, and (chemical process) engineering. Their most important areas of contribution are summarized in Table 5. This does not exclude possible and valuable contributions of applied microbiology. However, the latter could hardly address the sorption process aspects. More needs to be known regarding the composition of microbial and algal cell walls which are predominantly responsible for sequestering the metals. Interior of cells, due to its very 'dilute' nature seems to contribute very little to the overall metal uptake capacity of biomass.

Following equilibrium sorption and dynamic sorption studies, the quantitative basis for the sorption process is established, including process performance models. The biosorption process feasibility is assessed for well-selected cases. It is necessary to realize that there are two types of pilot plants to eventually be run hand in hand:

- Biomass processing pilot plant;
- Biosorption pilot plant.

The biomass supplies need to be well secured. That, in turn, brings the 'whole world' into the picture whereby it may become attractive for developing countries with biomass resources to participate in further development of the new biosorption technology.

Table 5
Areas of science discipline contributions

Chemistry
Biosorption mechanisms
Analytical methodologies
Instrumental analyses
Solution chemistry
Cell-wall composition
Sorption optimization on a molecular level
Engineering
Sorption equilibria
Dynamic flow sorption
Process optimization
Process feasibility and scale-up
Biosorption applications (Pilot 1)
Biosorbent preparation (Pilot 2)

3. Biosorption enterprise

Biosorption process of metal removal is capable of a performance comparable to its closest commercially used competitors, namely the ion exchange treatment. Effluent qualities in the order of only ppb (μg/L) of residual metal(s) can be achieved. While commercial ion exchange resins are rather costly, the price tag of biosorbents can be an order of magnitude cheaper (one-tenth the ion exchange resin cost).

The main attraction of biosorption is that it offers a great deal of cost effectiveness. While ion exchange can be considered a 'mature' technology, biosorption is in its early developmental stages and further improvements in both performance and costs can be expected.

Yes, biosorption can become a good weapon in the fight against toxic metals threatening our environment and our health. It is particularly in environmental applications where biosorption can make a difference due to its anticipated low costs. Needless to say, there may be many other applications on the horizon—wherever heavy metals need to be extracted from relatively dilute solutions. The application aspect is what makes the R&D work in this novel area exciting and worthwhile. While the biosorption process could be used even with a relatively low degree of understanding of its metal-binding mechanisms, better understanding will make for its more effective and optimized applications. There is a scientific challenge in revealing the basis of the metal biosorption phenomenon.

Despite the relative simplicity of the biosorption process, the technology based on it is as yet unproven and for its field success it requires continued R&D efforts. When it comes to client-specific applications, it is essential to realize that industrial effluents can differ from each other a great deal even though the technological processes where they originate may be turning out similar end-products. Close collaboration with each ‘client’ industrial operation is absolutely mandatory, requiring a broader background and understanding of the manufacturing procedures involved upstream. This is a typical consulting–engineering type of approach. Engineering skills become quite important because it is a process that one ends up dealing with. Biosorption becomes only one of the technologies potentially available for the effluent problem remediation.

In order to prevent failures in attempts to introduce the biosorption process as a viable and working alternative clean-up technology, close collaboration with the client is essential. A thorough test program using the real effluent becomes mandatory. However, this all should be based on adequate understanding of biosorption principles, mechanisms and materials. Procedures involved in this represent an outstanding challenge emphasizing the necessity of interdisciplinary collaborations.

There is little doubt that the combined environmental pressures, reflected in regulatory statutes, and economic stimuli make the removal and recovery of heavy metals from industrial effluents an important and ever-increasing priority which represents an extraordinary business opportunity coupled with an exciting scientific challenge.

When it comes to a new “biosorption” enterprise, to grow from the knowledge and know-how acquired in the process of scientific investigations providing the basis for the technology development, there are two aspects to such:

1. the new family of products: biosorbents;
2. the services involved in:
   - assessing the type of a problem to be remedied,
   - assessing the applicability of biosorption,
   - developing a customized biosorption process,
   - designing and building the plant,
   - eventually even operating the effluent treatment process, and even
   - recovering the metal(s) for resale/reuse.

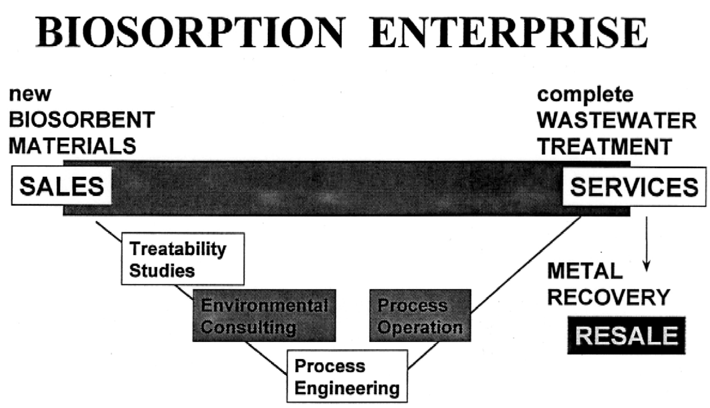

Fig. 6. An enterprise based on the new technology of metal biosorption can cover a wide range of activities from full “pollution control service” on one side to just selling the new family of biosorbents to clients. Metal recovery/resale constitutes the revenue-generating side-line activity.

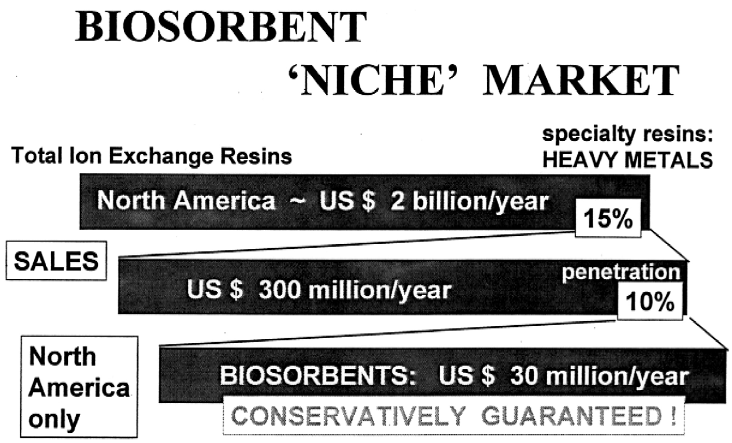

Fig. 7. The immediate potential market niche for biosorbent materials can be estimated as a likely fraction of their penetration into the currently existing sales of "specialty" ion exchange resins. In addition, competitive low-cost new biosorbents might open up vast new, currently untapped, environmental markets.

Obviously, it is not a small feat to develop a business venture along these broad lines. This is perhaps why the commercialization of biosorption technology has been so relatively slow and painful for those few who attempted it. However, the potential is undoubtedly there. The schematics of the biosorption enterprise involvement is seen in Fig. 6.

It is perhaps worthwhile mentioning that some sources put the current and established ion exchange resin sales in the order of maybe US$2 billion/year in North America alone. While ion exchange resins are considered a commodity on the market, the actual sales figures are not reliably available. World-wide sales are perhaps approximately quadruple the above figure for North America. However, only about 15% of the total ionex resin sales are for the specialty use such as heavy metal removal. Considering that only 10% of this volume could be 'stolen', or as the more commercial term goes 'penetrated' by (cheaper!) biosorbents, one is looking at the most conservatively estimated immediate and existing market for new biosorbent materials in the order of at least US$30 million only in North America (Fig. 7).

It can easily be envisaged that cheaper biosorbents would open up new, particularly environmental, markets so far non-accessible to ion exchange resins because of their excessive costs which make them prohibitive for clean-up operation applications.

As with any new technology, the essential need for continuing and strong R&D work in the field of biosorption cannot be overemphasized.

References

[1] S.C. Gilfillan, Lead poisoning and the fall of Rome, J. Occup. Med. 7 (1965) 53.
[2] B. Volesky, Evaluation of sorption performance,http://www.mcgill.ca/biosorption/publication/book/book.htm.
[3] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
[4] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.
[5] D. Kratochvil, B. Volesky, Biosorption of Cu from ferruginous wastewater by algal biomass, Water Res. 32 (1998) 2760–2768.
[6] I. Aldor, E. Fourest, B. Volesky, Desorption of cadmium from algal biosorbent, Can. J. Chem. Eng. 73 (1995) 516–522.
[7] J. Yang, B. Volesky, Intraparticle diffusivity of Cd ions in a new biosorbent material, J. Chem. Technol. Biotechnol. 66 (1996) 355–364.
[8] D. Kratochvil, B. Volesky, Multicomponent biosorption in fixed beds, Water Res. 34 (2000) 3186–3196.
[9] M.M.F. Figueira, B. Volesky, K. Azarian, V.S.T. Ciminelli, Multimetal biosorption in a column using *Sargassum* biomass, in: R. Amils, A. Ballester (Eds.), Biohydrometallurgy and the Environment Toward the Mining of the 21st Century (Part B): International Biohydrometallurgy Symposium—Proceedings, Elsevier, Amsterdam, The Netherlands, 1999, pp. 503–512.

[10] B. Volesky, S. Schiewer, Biosorption of metals, in: M. Flickinger, S.W. Drew (Eds.), Encyclopedia of Bioprocess Technology, Wiley, New York, 1999, pp. 433–453.
[11] S. Schiewer, B. Volesky, Ionic strength and electrostatic effects in biosorption of divalent metal ions and protons, Environ. Sci. Technol. 31 (1997) 2478–2485.
[12] J. Yang, B. Volesky, Modeling the uranium–proton ion exchange in biosorption, Environ. Sci. Technol. 33 (2000) 4079–4085.
[13] D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and hexavalent chromium by seaweed biosorbent, Environ. Sci. Technol. 32 (1998) 2693–2698.
[14] E. Fourest, J.C. Roux, Heavy metal biosorption by fungal mycelial by-products: mechanism and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.
[15] S. Schiewer, B. Volesky, Modeling of multi-metal ion exchange in biosorption, Environ. Sci. Technol. 30 (1996) 2921–2927.
[16] D.R. Crist, R.H. Crist, J.R. Martin, J. Watson, Ion exchange system in proton–metal reactions with algal cell walls, in: P. Bauda (Ed.), Metals–Microorganisms Relationships and Applications, FEMS Symposium Abstracts, Metz, France, May 5–7, Societe Francaise de Microbiologie, Paris, France, 1993, 13.
[17] R.H. Crist, J.R. Martin, D. Carr, J.R. Watson, H.J. Clarke, D.R. Crist, Interaction of metals and protons with algae: 4. Ion exchange vs. adsorption models and a reassessment of Scatchard plots; ion-exchange rates and equilibria compared with calcium alginate, Environ. Sci. Technol. 28 (1994) 1859–1866.
[18] M.E. Treen-Sears, M.E. Martin, B. Volesky, Control of *Rhizopus* biosorbent's quality during propagation, in: R.W. Laurence, R.H.N. Branion, H.G. Ebner (Eds.), Fundamental and Applied Biohydrometallurgy, Elsevier, Amsterdam, The Netherlands, 1986, pp. 305–308.
[19] Z.R. Holan, B. Volesky, Accumulation of cadmium, lead and nickel by fungal and wood biosorbents, Appl. Biochem. Biotechnol. 53 (1995) 133–142.
[20] B.E. Holbein, Immobilization of metal-binding compounds, in: B. Volesky (Ed.), Biosorption of Heavy Metals, CRC Press, Boca Raton, FL, 1990, pp. 327–340.
[21] G.W. Bedell, D.W. Darnall, Immobilization of nonviable, biosorbent, algal biomass for the recovery of metal ions, in: B. Volesky (Ed.), Biosorption of Heavy Metals, CRC Press, Boca Raton, FL, 1990, pp. 313–326.
[22] J.A. Brierley, Production and application of a *Bacillus*-based product for use in metals biosorption, in: B. Volesky (Ed.), Biosorption of Heavy Metals, CRC Press, Boca Raton, FL, 1990, pp. 305–312.
[23] C.L. Brierley, J.A. Brierley, Immobilization of biomass for industrial application of biosorption, in: A.E. Torma, M.L. Apel, C.L. Brierley (Eds.), Biohydrometallurgical Technologies, Proceedings of the International Biohydrometallurgy Symposium, The Minerals, Metals and Materials Society, Warrendale, PA, 1993, pp. 35–44.
[24] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biosorption column, Water Res. 31 (1997) 2327–2339.
[25] M.M. Figueira, B. Volesky, V.S.T. Ciminelli, F.A. Roddick, Biosorption of metals in brown seaweed biomass, Wat. Res. 34 (2000) 196–204.
[26] N. Kuyucak, Feasibility of biosorbents application, in: B. Volesky (Ed.), Biosorption of Heavy Metals, CRC Press, Boca Raton, FL, 1990, pp. 371–378.
[27] C.D. Gilson, A. Thomas, Calcium alginate bead manufacture: with and without immobilised yeast. Drop formation at a two-fluid nozzle, J. Chem. Technol. Biotechnol. 62 (1995) 227–232.
[28] T.H. Jeffers, P.G. Bennett, R. Corwin, Biosorption of metal contaminants using immobilized biomass—field studies. Report of Investigations, U.S. Bureau of Mines, Salt Lake City, 1993.
[29] E.M. Trujillo, T.H. Jeffers, C. Ferguson, H.Q. Stevenson, Mathematically modeling the removal of heavy metals from wastewater using immobilized biomass, Environ. Sci. Technol. 25 (1991) 1559–1565.
[30] T.M. Chang, Artificial cells with emphasis on bioencapsulation in biotechnology, Biotechnol. Annu. Rev. 1 (1995) 267–295.
[31] T.M. Chang, Artificial cells in immobilization biotechnology, Biomater., Artif. Cells, Immobilization Biotechnol. 20 (1992) 1121–1143.
[32] A. Leusch, Z.R. Holan, B. Volesky, Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae, J. Chem. Technol. Biotechnol. 62 (1995) 279–288.
[33] J. Yang, B. Volesky, Biosorption and recovery of uranium by seaweed biomass, in: R. Amils, A. Ballester (Eds.), Biohydrometallurgy and the Environment Toward the Mining of the 21st Century (Part B): International Biohydrometallurgy Symposium—Proceedings, Elsevier, Amsterdam, The Netherlands, 1999, pp. 483–492.