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Review Article

THE RATIONALE, SCOPE, SCIENTIFIC VALUE AND FUTURE POTENTIAL OF BIOSORPTION RESEARCH AS AN INDUSTRIAL PROCESS: A CRITICAL REVIEW

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ABSTRACT

Adsorption operation has been commercialized in an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, ease of operation and efficiency. Biosorption, which is simply defined as the removal of substances from solution by material of biological origin; is a physio-chemical process which includes mechanisms such as, surface complexation, ion-exchange, absorption, precipitation and adsorption. Biosorption research concerns mainly metals and related substances, but now this term is applied to particulates and all manner of organic substances as well. Though the research publication on biosorption increases continuously, it is pathetic to note that there has been literally no exploitation in an industrial context. This article on biosorption research critically reviews aspects regarding the rationale, scope, scientific value and future potential of biosorption research as an industrial process.

INTRODUCTION

Detection and treatment of toxic metals, metalloids, radio nuclides and various organic pollutants in industrial effluents is of great importance to any chemical industry to fulfill ongoing strict regulations of the pollution control board. One obviously has no option but to prevent or limit pollutant discharges to avert the threat to ecosystems and human health.

The metal removal from aqueous solutions often leads to effective metal concentration. Rather than the slow natural process of metal mineralization, the effective removal is attained only when the metal becomes concentrated to the point that it can be either sold or returned to the process. This aspect of the operation deals with the potential recovery of the metal, which should go hand in hand with the removal aspect, making the overall process ultimately effective for controlling the metal utilization in the technological processes designed by humans.
Various methods of treatment for industrial wastewater have been reported in the literature[1]. Amongst these methods are precipitation, neutralization, adsorption and ion-exchange. The process of adsorption implies the presence of an "adsorbent" solid that bind molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is cheap, available in large quantities, and easily regenerable[2].

In general, the sorption capacities of raw lignocellulosic biosorbents were increased by modifying them by various methods because it is believed that metal ion binding by lignocellulosic biosorbents take place through chemical functional groups such as amino, carboxyl, or phenolics. To develop new adsorbents and improve existing adsorbents great effort has been contributed recently. The feasibility of using low-cost agro-based waste materials was studied by many investigators[3-13].

Basically all bioadsorbents has an affinity for metal species and a depth of various researches exists with plant and animal biomass as well as micro-algae and derived products. Mostly biosorption research concerns metals and related substances. Published research on biosorption is continuing to increase dramatically.

This article on biosorption research critically reviews aspects regarding the rationale, scope, scientific value and future potential of biosorption research as an industrial process.

Biosorbents

The various biomass potentially available for biosorption purposes are enormous, since all biosorbents have an affinity for metals, and indeed other pollutants. All kinds of plant, animal and micro-algae biomass, and derived products, were investigated for a variety of substances in a variety of

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forms[14,15]. A common rationale for such studies is to identify highly-efficient biosorbents that are cheap. In theory, these would, provide new opportunities for pollution control, element recovery and recycling. A flow in this approach is that biomass composition does not vary significantly between different species of the same genres. Cell wall structure and composition does not vary significantly between different species of the same genres. Cell wall structure and composition is similar throughout all grain positive and negative bacterial, algal and plant material, although there are some differences between major genre[16, 17, 18].

Since we have already studied so many representative organisms, there seems little justification in examining yet more different fungal, bacterial, algal and plant species for remarkable new properties. There also seems no point in examining systems which could never be applied in an industrial context like rare or endangered plants, pathogenic bacteria and fungi. Perhaps research should employ those biomass types that are cheap, efficient, and easy to grow or harvest and most importantly concentration be given to biomass modifications, physico- chemical conditions and alteration of bioreactor configuration to improve biosorption.

Various low-cost abundantly available adsorbents were used and investigated: agricultural wastes such as coffee[19] and tea waste[20], red fir[26], peanut hull[3,24], hazelnut shells[21,22,23], pinus bark[30-33] and different bark samples[34-43], and maple[27], saw dusts[28,29], coconut husk[45,46] and palm kernel husk[44], corncobs[51], peanut skins[47], and rice hulls[53], coffee grounds[55], apple wastes[54], bark[56,57], wool fibers[58], wool and tea leaves[59], pine needles, olive cake , cactus leaves , almond shells, banana peels, charcoal[60] and orange peels[63], maize leaf[74] and palm fruit bunch[65].

Derivatives with modified metal binding abilities and affinities were created by chemical modification of biomass[75,76,77]. Modified cellulosic materials[48,49] ,modified lignin[61,62], modified corncob[52], chemically modified cotton[50] , modified bark[78], modified sun flower stalk[7], modified sugar beet pulp[64] , were used and investigated.

The disadvantages of using freely suspended microbial biomass include small particle size, poor mechanical strength and difficulty in separating biomass and effluent. These can be minimized by using immobilized biomass particle in packed or fluidized bed reactors[14,79-83].

Biosorbents in column application

Bio-films, the immobilized living biomass on supports prepared from a range of inert materials have been used in a variety of bioreactor configurations, including trickle filters, rotating biological contactors, fixed bed reactors, air-lift bio reactors and fluidized bed reactor[84,85]. In addition to the use of bio films, living or dead biomass of all microbial groups has been immobilized by cross-linking or encapsulation. Supports include agar, alginates, silica gel, cellulose, cross-linked ethyl acrylate-ethylene glycol demethylacrylate, polyacrylamide, and the cross linking reagents glutaraldehyde and toluene diisocyanate[81,82,86].

In the standard sorption process, one cannot use biomass of any kind directly. Without reinforcement and granulation, biomass is very soft and hence cannot be used in column operations. Early attempts of immobilization were carried out by the cross linking of Penicillium Sp. with urea-formaldehyde mixture[87,88,89].

According to the formation of esters or ethers of the natural biopolysaccharides present in the biomass, cross-linking could be classified. Esters could be formed via acid anhydrides (phthalic, maleic and succinic anhydrides), acid chlorides of dicarboxylic acids (from succinyl to sebacoys), diisocyanates, dicarboxylic acids, and cross-linking of polysaccharide derivatives (includes modification by the introduction of new reactive groups for new types of covalent bonds or by the formation of new substrates which would be cross-linked with a system, already known.): reactions with mercapto groups; reactions with unsaturated compounds ; reactions with dialdehyde or with modified polysaccharide with diamines, alkanedithiols, hydrazides, disulfides, etc.; reversible cross-links contains disulfide groups. Ethers could be formed via aldehydes (formaldehyde,acrolein,dialdehydes),N-hydroxymethyl compounds (amides, carbamates, ureas, triazine) activated vinyl compounds (acryl amides, diethenyl sulfone, crotonates and vinyl ketones) epoxy and aziridinyl compounds (diepoxides, 1-chloro-2,3-epoxypropane, triaziridinly, phospine oxide, dihalohydrins, and reaction products of ethylene imine with bis (chloroformate), acid chlorides of diisocyanates, dicarboxylic acids, etc.),disulfonate esters of polymethylene diols, bifunctional aliphatic chlorides, and bis(diazo) alkanes.

Originating from dialdehydes, the free aldehydic groups could be used for cross-linking only after the reduction of metal ions and the oxidation of aldehydic groups to carboxyl groups, and hence possibly increase the biosorption capacity of a prepared biosorbent.

Modified cellulosic materials[90] like phosphated sawdust tested, demonstrated that processed biomass could be successfully employed in sequestering metals. To illustrate the biomass transformation into a better metal-sorbent and to show the possibility of studying different metal-sequestering functional groups and metal uptake mechanisms, sawdust was oxidized to oxo and carboxy forms and tested for the introduction of carboxymethyl and sulfoethyl groups.

In the reinforcement of any kind of biomass, there are suitable cross linking procedures that could be used. Though, there may be a limitation in the first step of cross linking: alkaline or acidic conditions required for the reaction to proceed are usually very strong. The durability of different cross-linked biosorbents to extreme acidic and alkaline conditions has been studied only to a limited extent[91]. Another limitation for cross-linked biosorbents may relate to the pH range in which they should eventually work, this understanding could relate not only to the metal sorption operations but also to the desorption operations.

In the actual sorption process, the cross-linked biosorbents have to feature a controlled, porosity and uniform size apart from swelling characteristics and rigidity to meet the process requirements relating to mass transfer characteristics of the material. These aspects along with the variable nature of the raw biomass types already identified for their exciting metal adsorbing capabilities represent an outstanding research and development challenge.

Exploitation potential & competing technology

The rationale for the work to be carried out in the area of biosorption is often based on the apparent exploitation potential often cited in the literature. Quoted as a low cost treatment method and as a suitable option where a 'low tech' approach is sufficient, biosorption is a potential area for exploitation in the recovery of precious metals such as gold, palladium and platinum though it is known for the detoxification of pollutant metals. Less work is done in the recovery of precious metals.

There is no significant commercialization of biosorption technology as given in many review and research papers from various countries. Only at pilot scale, some biomass based systems have been evaluated. Being termed as pseudo-ion-exchange processes[92], Biosorption is often non-selective meaning that application to metal mixtures would be problematic. Ion-exchange resins are much more predictable for a given metal ion, and are more suitable for selective recovery of target substances. The lack of specificity and lower robustness of biomass-based systems are often cited as major reasons that limit the commercialization of biosorption[92]. Also suspended biomass is not durable and effective in continuous application[93]. Immobilized biomass preparations may overcome the robustness issue, but did not overcome the specificity problem. Also biosorption technology transfers the adsorbate from one medium to another, but the safe disposal of loaded biosorbent, recovery of adsorbate, and regeneration of the biosorbent are still under question.

Ion exchange, chemical precipitation, reverse osmosis, oxidation/reduction methods, solvent extraction and solid/liquid separation are some of the common procedures employed for removing metal ions from waste streams. The choice of the process used depends on the target effluent concentrations and the substances to be treated. Some processes like precipitation and ion exchange are predictable and well understood and have been commercialized and are being incorporated into many industrial processes[92].

Some of the disadvantages in the conventional metal removal methods are generation of toxic sludge, incomplete metal removal, high energy and reagent requirements. These serve as the basis for arguments supporting biosorption[14,92,94]. But though proposed to see a big breakthrough, yet, ironically has probably seen no success in exploitation.

CONCLUSION

Biosorption has been proposed as a cheap and effective biotechnology for many years, yet has had extremely limited industrial exploitation to date, even as an addition to conventional pollutant treatment approaches in hybrid technologies. Biosorption is frequently compared with ion-exchange technology[85,80,92] and often stated to provide a cheaper alternative[80]. Though specificity is a problem, the life cycle of biosorbents are also shorter[80]. Identification of better and more selective biosorbents, more development of biosorption models and identification of biosorption mechanisms are some common suggestions for future research directions[85]. After so many years of research in biosorption, it is debatable whether any more efforts in these directions will result in significant developments or novel contributions to understanding. The development of specific metal-binding molecules and engineered highly-specific biosorbents was heralded as a promising research direction, although there seems to have been little progress in industrial application. The general view seems speculative in the specificity of biosorption for both organic and inorganic substances, hence it can be concluded that the rationale for biosorption studies is rather weak, especially if based on commercial development and application, instead the importance of biosorption in the environment and conventional biotreatment processes perhaps suggests further research should be directed in these areas.

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