Preface

Biotechnology–Materials Interface

Even though significant research advancements have been made in the area of biotechnology as applied to agriculture, human health and drug design, enough awareness of the role of biology in the area of materials and metals is not evident. The biology–materials interface encompasses a wide spectrum of opportunities and applications relevant to development and processing of modern materials.

The new millenium rightly belongs to biotechnology and rapid progress in materials science based on biological principles is round the corner. Materials processing by microorganisms is reported to have begun almost 3.5 billion years before human intervention. Over geological periods of time, the tiny earthly microorganisms have evolved to provide process energy, use waste metal compounds, produce enormous quantities of valuable minerals and live in hostile environments.

Biotechnology/materials interface is of relevance in a number of emerging interdisciplinary areas such as biogenesis and biomineralization, biomaterials processing and biomimetics, ceramics and biomedical engineering, bioleaching, biocorrosion, biofouling and biodeterioration, and bioenvironmental control.

A tiny microbial cell incorporates in itself amazing processing functions such as metal ion accumulation, generation and synthesis of polymers and mineral composites and synthesis of a variety of biopolymers and catalysts. Sensors, regulators and adaptive machinery associated with microorganisms make them akin to a modern, microprocessor-controlled biochemical factory. With the advent of genetic engineering, it has become possible to modulate microorganisms so as to perform a desired function at faster rates. For example, metal resistance in bacteria is known to be plasmid mediated and it may become possible to develop 'super bugs' through plasmid transfer.

Biological systems in nature are replete with examples of organic and inorganic supramolecular assemblies and superior architectural styles. Unique and exquisite biominerals such as diatoms, coccoliths, seashells and bones exhibit controlled processing with respect to structure, size, shape, orientation and texture. Tough, durable and adaptive polymer–ceramic composites are fabricated under natural conditions through biological routes. There is a strong interrelationship between biomineralization and materials chemistry based on biomimetics and molecular tectonics.

In nature, microbes participate in lithification, mineral formation, conversion, precipitation and transport as well as in mineral diagenesis and sedimentation. Metal–microbe cycles in nature are responsible for the various biochemical and geochemical reactions leading to the formation of mineral deposits. Among the essential elements required for living organisms, carbon, oxygen, hydrogen, silicon, magnesium, phosphorus, calcium, iron and manganese are common ingredients of biominerals. There is a predominance of calcium biominerals. Many elements such as copper, zinc and lead are deposited on the external surfaces of bacteria as sulfides. Biomineralization takes place in well-defined spatially delineated sites and intimate association of inorganic and organic phases is its hallmark. Biomineralization involves molecular construction of discrete, self-assembled, organic supramolecular systems. Four constructional processes, namely, supramolecular preorganization, interfacial molecular recognition, vectorial regulation and cellular processing have been recognised. Biomimetic approaches to the crystal engineering of inorganic materials involves strategies such as templating, directed growth and microstructural fabrication to develop different products like shaped composites, textured crystals and polymer–mineral composites. Possibilities of modifying crystal shapes by the interaction of soluble molecules with crystal faces do exist. Crystal formation can either by promoted or inhibited biologically.

There are more than 50 recorded biominerals which include various metal carbonates, phosphates, halides, oxalates, oxides and sulfides. Elemental selenium, tellurium, gold, silver, sulfur and mercury are biogenic. Minerals are generated by most groups of organisms such as bacteria, fungi, algae and plants. Scale of biogenic production in comparison to human usage is indeed staggering. For example, the biogenic generation rate for $CaCO_3$ is estimated to be about 5×10^{12} kg/annum and that of SiO_2,, 5×10^{11} kg/annum. Structurally ordered materials in nature are produced by higher organisms such as mollusks. Structural polymer/mineral composites are composed through a polymer framework. Extracellular microstructures resembling a brick wall with the mortar (polymer) laid before the ordered bricks of calcium mineral are assembled. Elegant structures of silica and iron oxides are biologically constructed.

Humans could mimic biogenesis to manufacture special materials. Examples are colloidal platinum (catalyst). Synthesis of CoS, AgCl and Fe_3O_4 from amorphous materials can be achieved. Biogenic coating process to form amorphous or microcrystalline coatings such as sealing of cement by $CaCO_3$ and deposition of mineral surfaces on metals and alloys have become practical.

In recent years, there has been growing interest in biological ceramics such as those found in bones, teeth and shells. Synthetic organic compartments are now used to form inorganic nanoparticles with precisely controlled shapes and sizes. Net shape, high-density ceramics with layered microarchitectures are now formed by sequential deposition techniques. Techniques in biomimetic ceramic processing include compartmentalized processing, thin-film formation and net-shape formation with layered architectures.

The microorganism, *Thiobacillus ferrooxidans,* which is known to be effective in the leaching of several minerals was first isolated in the laboratory in 1947 from the acid mine drainage of bituminous coal mines. Throughout the world, bioleaching processes are now being increasingly used as alternative and supplementary methods because high-grade ore reserves are getting continuously depleted and energy costs are increasing. Moreover, environment conservation is an all-embracing issue. Biohydrometallurgical extraction of metals from a wide variety of ores is being commercially practised all over the world. Large quantities of copper, uranium and gold ores are processed by microbial technology on an industrial scale. The recovery of several other metals is also possible by such methods.

Microorganisms inhabiting ore bodies and water systems can also play a significant role in causing environmental pollution, such as acid water generation. At the same time, appropriate usage of various microorganisms can also bring about environmental protection. Acidic waters originating from bacterial sulphidic mineral oxidation, especially from metalliferrous and coal mines, constitute a major environmental pollution problem. Both active and abandoned mines remain a source of this problem termed, acid mine drainage (AMD) leading to contamination of ground water tables, rivers, streams and even sea coasts. In nature, both iron and sulphur-oxidising *Thiobacillus* group of bacteria are associated with mineral sulphides such as arsenopyrite, pyrite, chalcopyrite, sphalerite, galena, molybdenite, millerite, orpiment and antimonite, all of which serve as energy sources for the microbes. The abundance of iron and sulphur in natural sulphide mineralization makes it easier for the *Thiobacillus* group of bacteria to colonise on them. Biooxidation of pyrite and sulphur leads to the formation of sulphuric acid containing Fe^{+++} which subsequently dissolve various toxic metal ions through its solvent action.

The following features of microorganisms are significant in detoxification of liquid and solid effluents from mining and mineral processing industries.

(a) Removal of dissolved metal ions even at low ppm levels

(b) Concentration of accumulated metals for recovery

(c) Degradation of toxic organic chemicals from effluents to inert products

At least four major mechanisms have been known for biological removal of metal ions from liquid effluents, namely, bioadsorption, bioaccumulation, precipitation and volatilization. In biodegradation, the microorganisms transform the organic chemicals into innocuous forms, degrade them to carbon dioxide and water, besides decomposing them anaerobically. Biosorption is primarily an adsorption-type phenomenon taking place through electrostatic attraction of metal cations to the negatively charged cell surfaces. Moreover, the chemical composition of the bacterial cell wall also plays a role in biosorption through metal binding to exopolysaccharides, proteins and other functional groups. Bioaccumulation is the process of metal uptake by living microorganisms, dependent on metabolic energy. This requires specific transport systems and depends on metal tolerance of the organisms. Inter- as well as intracellular accumulation can occur.

The involvement of microorganisms in the deterioration and destruction of materials can be characterized by three different terms, namely, biofouling, biodeterioration and biocorrosion or microbiologically induced corrosion. The above terms though different in nature, could be complementary in their ultimate consequences. Biofouling generally refers to adherence of micro- and macro-organisms onto material surfaces in marine and freshwater systems leading to formation of fouled layers. Deterioration of nonmetallic materials such as glass, concrete, cement, rubber, wood, plastics and some organic and inorganic fluids in the presence of microorganisms is termed biodeterioration. Corrosion of metals and alloys induced by the activities of microorganisms is defined as bio- or microbial corrosion. Fouling involves the undesirable formation of inorganic and organic deposits on surfaces resulting in unsatisfactory equipment performance and shortening its lifetime. Accumulation and growth of living organisms along with their metabolic and reaction products on material surfaces occur in aquatic systems–fresh and seawater. The fouling ecosystem consists of various components such as organic molecules, bacteria, microfungi, protozoa, algae and invertebrates. Colonization of aquatic organisms leads to development of tenacious biofilms on surfaces. Biodeterioration of wood is a problem of marine environments. Besides, these phenomena include borers in cement, plastics and other materials, surface fouling of ships, buoys, rafts and intake tunnels.

Microorganisms are omnipresent in nature and their ability to grow and reproduce at amazingly rapid rates account for their presence in soil, water and air. Micro- and macro-organisms exhibit extreme tolerance to hostile environments such as acididc and alkaline pH, low and higher temperatures as well as pressure gradients. In microbial corrosion processes, aggressive environments are generated by microorganisms, several interaction factors participating in the mechanisms. The microorganisms often make a contribution without being solely responsible for the failure of materials. In this respect, the microbes can be viewed as living catalysts.

The role of biology in materials processing is highlighted in the special issues of the *Journal of the Indian Institute of Science* in three parts covering,

(a) Mineral biodissolution and biometal tolerance
(b) Biofilms and biomaterials and
(c) Biofouling and biocorrosion.

Most of the areas falling at the interface between biology and metals/materials are covered in this attempt. Technical papers for the purpose were invited from scientists working in leading scientific organisations in the country. The response from the authors was overwhelming and I am thankful to all of them.

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