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생물흡착제의 고정화 방법에 대한 고찰

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Review for Immobilization Methods of Biosorbent

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ABSTRACT

Immobilization of biosorbent is very important for application to real wastewater treatment process because biosorbent itself does not have enough tough structure. Therefore, resent research on heavy metal biosorption using biomass has been focused on its efficient immobilization method. To improve the mechanical strength of freely biosorbent, many immobilization methods have been suggested for applications to the biosorbent such as microorganisms or polysaccharides. In this study, various immobilization methods such as adsorption, covalent binding, entrapment, encapsulation, and crosslinking will be introduced.

Keywords : Adsorption, Biosorption, Entrapment, Immobilization

초록

생물흡착제는 그 자체만으로 실제폐수처리에 적용하기에는 충분하지 못한 구조를 가지고 있기 때문에 고정화는 매우 중요하다. 그래서 최근의 연구는 생물흡착제를 효과적으로 고정화시키는 방법에 초점이 맞추어져 있다. 미생물이나 다당류와 같은 생물흡착제의 기계적 강도를 향상시키기 위하여 지금까지 많은 고정화 방법이 제안되어 왔다. 본 연구에서는 다양한 고정화 방법들(adsorption, covalent binding, entrapment, encapsulation, and crosslinking)을 소개하고자 한다.

핵심용어 : 흡착, 생물흡착, 포괄법, 고정화

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1. 서 론

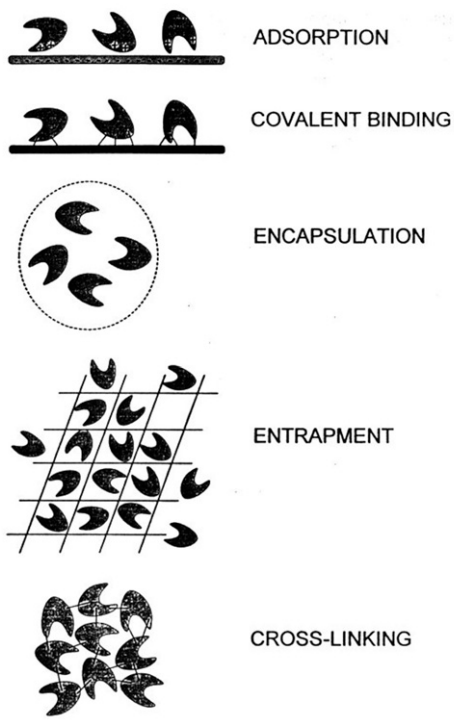
Biosorption of heavy metals by certain types of biosorbent can be promising alternative for removal of heavy metal from wastewater or contaminated ground water. Immobilization of biosorbent is required for application to real wastewater treatment process because biosorbent itself does not have enough tough structure. Unfortunately, free biosorbents are not suitable for use as a column packing since the free biosorbents tend to clump together and excessive hydrostatic pressure are required in order to generate suitable flow rates. Furthermore, since free biosorbents are inherently fragile, high pressure may cause disintegration of the free biomass. The fragility problem has been alleviated by the immobilization of the biomass within a suitable porous matrix. Many immobilization methods have been suggested for applications to the biomass such as microorganisms or polysaccharides. The schematic diagram of immobilized biosorbents can be shown as [Fig. 1] In this study, various immobilization methods will be introduced.

2. 실험재료 및 방법

2.1 Adsorption

Immobilization by adsorption is the simplest method and involves reversible surface interactions between enzyme/cell and support material. The forces involved are mostly electrostatic, such as van der Waals forces, ionic and hydrogen bonding interactions, although hydrophobic bonding can be significant. These forces are very weak, but sufficiently large in number to enable reasonable binding. For example, it is known that yeast cells have a surface chemistry that is substantially negatively charged so that use of a positively charged support will enable immobilization[1]. Existing surface chemistry between the biosorbents and support is utilized so no chemical activation/modification is required and little damage is normally done to biosorbents in this method of immobiliz ation. Among the advantages are as follows:

- ◆ Little or no damage to biosorbents.
- ◆ Simple, cheap, and quick to obtain immo bilization.
- ◆ No chemical changes to support or biosor bents.
- ◆ Reversible to allow regeneration with fre sh biosorbents.



[Fig. 1] Schematic diagram of immobilized biosorbents.

Disadvantage include:

- ◆ Leakage of biosorbents from the support/ contamination of product.
- ◆ Nonspecific binding.
- ◆ Overloading on the support.
- ◆ Steric hindrance by the support.

2.2 Covalent Binding

This method of immobilization involves the formation of a covalent bond between the biosorbents and support material. The bond is normally formed between functional groups present on the surface of the support and functional groups belonging to amino acid residues on the surface of the biosorbents. A number of amino acid functional groups are suitable for participation in covalent bond formation. Those that are most often involved are amino group (NH_2), carboxylic group (CO_2H), hydroxyl group (OH), and sulfhydryl group (SH). Many varied support materials are available for covalent binding, and the extensive range of supports available reflects the fact that no ideal support exists. Therefore, the advantages and disadvantages of a support must be taken into account when considering possible procedures for a given biosorbent immobilization[2]. Many factors may influence the selection of a particular support, and research work has shown that hydrophilicity is the most important factor for maintaining biosorbent activity in a support environment[3]. Consequently, polysaccharide polymers, which are very hydrophilic, are popular support materials for enzyme immobilization. For example, cellulose, dextran, starch, and agarose are used for biosorbent immobilization[4),5)]. Other popular supports for biosorbent immobilization are porous silica and porous glass. Porous silica consists of small spherical particles of silica fused together in such a way as to form microactivities and small channels. The support is normally sold in bead form, and is very strong and durable. Porous glass is also durable and resistant to microbial disintegration or solvent distortion. However, these two supports are less hydrophilic than the polysaccharide materials.

2.3 Entrapment

Immobilization by entrapment differs from adsorption and covalent binding in that biosorbent molecules are free in solution, but restricted in movement by the lattice structure of a gel. The porosity of the gel lattice is controlled to ensure that the structure is tight enough to prevent leakage of biosorbent, yet at the same time allow free movement of substrate and product. Inevitably, the support will act as a barrier to mass transfer, and although this can have serious implications for reaction kinetics, it can have useful advantages since harmful cells, polysaccharides are prevented from interaction with the immobilized biocatalyst. There are several major methods of entrapment:

- ◆ Ionotropic gelation of macromolecules with multivalent cations (e.g., alginate)
- ◆ Temperature-induced gelation (e.g., agar ose, gelatin)
- ◆ Organic polymerixation by chemical/ photochemical reaction (e.g., polyacrylami de)
- ◆ Precipitation from an immiscible solvent (e.g., polystyrene).

Entrapment can be achieved by mixing a biosorbent with a polyionic polymer material and then crosslinking the polymer with multivalent cations in an ion-exchange reaction

to form a lattice structure that traps the biosorbents[6)~8)]. Agar, polyacrylamide, alginate or kappa-carrageenan have been used for the entrapment of biosorbent. However, the mechanical strength of agar is rather weak. Acrylamide monomer is poisonous, so immobilization with acrylamide is of course deleterious for the biomass[9)]. Also, alginate gel has low mechanical strength and requires the addition of Ca^{2+} and Al^{3+} ions for stabilization of the gel. This procedure has a drawback because these ions form a precipitate with phosphate ion[10)]. On the other hand, KCl is required for the immobilization of κ-carrageenan, but this has the economical disadvantage of a high removal cost for λ-carrageenan, causing the gel to become weak[11)]. Consequently, it may be impractical to apply these polymeric materials to wastewater treatment as immobilization carriers.

The use of polyvinyl alcohol (PVA) as an immobilization carrier was initiated about 10 years ago[12)]. PVA is a raw material of vinylon and can be produced industrially rather cheaply. PVA also offers various advantages over the conventional immobilization methods, such as low cost, high durability and chemical stability and non-toxicity to viable cells. Up to now, several methods of immobilization using PVA have been reported[13)~15)]. Among them, PVA-boric acid method was widely used activated sludge was immobilized[14)]. However, this method has a problem of hydration of immobilized biomass. A significant development in this area has been the introduction of κ-carrageenan polymers that can form gels by ionotropic gelation and by temperature-induced phase transition, which has introduced a greater degree of flexibility in gelation systems for immobilization.

2.4 Encapsulation

Encapsulation of biosorbents can be achieved by enveloping the biological components within various forms of semi-permeable membranes[16)]. It is similar to entrapment in that the biosorbents are free in solution, but restricted in space. Many materials have been used to construct microcapsules varying from 10-100μm in diameter; for example, nylon and cellulose nitrate have proven popular. The problems associated with diffusion are more acute and may result in rupture of the membrane if products from a reaction accumulate rapidly. A further problem is that the immobilized biosorbent particle may have a density fairly similar to that of the bulk solution with consequent problems in reactor configuration, flow dynamics, and so on. It is also possible to use biological cells as capsules, and a notable example of this is the use of erythrocytes (red blood cells). The membrane of the erythrocyte is normally only permeable to small molecules. However, when erythrocytes are placed in a hypotonic solution, they swell, stretching the cell membrane and substantially increasing the permeability. In this condition, erythrocyte proteins diffuse out of the cell can diffuse into the cell. Returning the swollen erythrocytes to an isotonic solution enables the biosorbent membrane to return to its normal state, and the enzymes trapped inside the cell do not leak out. A distinct advantage of this method is co-immobilization. Cells and / or enzymes may be immobilized in any desired combination to suit particular applications.

2.5 Crosslinking

This type of immobilization is support-free and involves joining the cells to each other to form a large, three-dimensional complex

structure, and can be achieved by chemical or physical methods. Chemical methods of crosslinking normally involve covalent bond formation between the cells by means of a bi- or multifunctional reagent, such as glutaraldehyde and toluene diisocyanate. However, the toxicity of such reagent is a limiting factor in applying this method to living cells and many enzymes. Both albumin and gelatin have been used to provide additional protein molecules as spacers to minimize the close proximity problems that can be caused by crosslinking a single biosorbent[17]. Physical crosslinking of cells by flocculation is well known in the biotech nology industry and does lead to high cell densities. Flocculating agents, such as polyamines, polyethyleneimine, polystyrene sulfonates, and various phosphates, have been used extensively and are well characterized. Crosslinking is rarely used as the only means of immobilization because the absence of mechanical properties and poor stability are severe limitations. Crosslinking is most often used to enhance other methods of immobi lization, normally by reducing cell leakage in other systems.

3. 결론

Compared with freely suspended biosor bents, immobilized biosorbent systems could provide many advantages, which include efficient and effective regeneration and reuse of the biosorbent, easier solid-liquid separation and minimal clogging in continuous flow systems. Up to now, entrapment was widely used among many immobilization methods. However, to apply the actual treatment system, other methods should be improved. Furthermore to compete commercial ion-exchange resin, adsorption capacity as well as mechanical strength of immobilized biosorbent should be developed together.

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