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Industrial waste derived biosorbent for toxic metal remediation: Mechanism studies and spent biosorbent management

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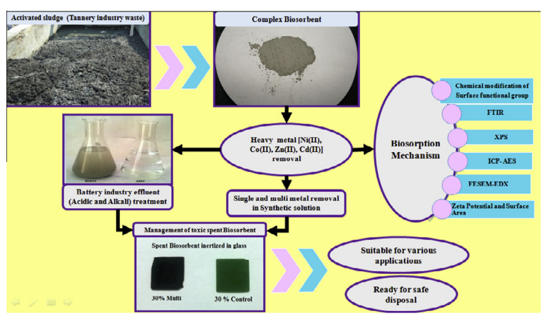
HIGHLIGHTS

- Tannery industry waste sludge as complex biosorbent for heavy metal removal.
- Multi-metal removal in real effluent of battery manufacturing industry.
- Management of spent biosorbent in productive form as phosphate glass.
- >30% metal bearing biosorbent was successfully inertized as good glass.
- Elucidation of mechanism by functional group modification, FTIR, XPS, ICP test.

GRAPHICAL ABSTRACT



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ABSTRACT

The dried activated tannery industry sludge was used as complex biosorbent for removal of Ni(II), Co(II), Zn(II) and Cd(II) in single and multi-component system. The mechanism for toxic metals biosorption was analyzed along with equilibrium isotherm and kinetic study. The efficiency of the biosorbent was studied for real effluent treatment. Further, safe disposal of the spent biosorbent in glass form was established which is significant for commercial implementation of the biosorption technology. Zn(II) and Cd(II) showed 99% removal within 10 min while Ni(II) and Co(II) attained 98% removal at 20–24 h. The biosorbent showed >96% removal efficiency for these metals in effluents from battery manufacturing industry with simultaneous removal of Pb, Cu and Fe ions. Chemical modification of hydroxyl, carboxyl, amino, phosphate, sulfonyl and carbonyl functional groups were undertaken and surface characterization of the biosorbent was done using zeta-potential, FTIR, FESEM-EDX and XPS technique to elucidate the biosorption mechanism. The biosorption efficiency was found to decrease significantly indicating involvement of functional groups in metal binding which was confirmed by FT-IR. Rapid removal of Zn (II) and Cd(II) was due to binding with functional groups. However, the gradual removal of Ni(II) and Co(II) was governed by ionic exchange mechanism, confirmed by ICP-AES. Deconvolution of N1s and C1s XPS spectra produced two and one additional peaks respectively, suggesting formation of amino-metal complexes. Increase in atomic concentration of total oxygen explained further the formation of different metal complexes on biosorbent surface. Upto 30% of metal laden biosorbent could be inertized in phosphate glass matrix as confirmed by the XRD-analysis. No leaching of heavy metals was observed on the glass with thermal cycle at 75 °C for 8 h/day up to 35 days.

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1. Introduction

Heavy metals contamination in water is an important socio-environmental issue. Heavy metals are non-biodegradable, non-thermodegradable and readily accumulate in living organism that associate negatively with health and ecosystem. They are persistent in nature and therefore, very difficult to eliminate naturally from the environment, even for trace amounts. Intensive anthropogenic activities involving domestic, transportation, and industrial development are associated with the population growth and subsequent enhancement in the heavy metal pollution towards the environment that have considerable influence on human health [1]. Zn, Cd, Ni, Pb, Cr, Co and Cu are several general types of pollutants found in the wastewater of large and small scale industries such as electroplating, welding, tanneries, batteries, mining operations, iron and steel, smelting, electrolysis, electrical appliance manufacturing, paper and pulp, fertilizer and pesticide and alloy industries.

The efficiency of various processes have been investigated to eliminate heavy metals from water and wastewater, such as chemical precipitation, electrochemical treatment, membrane processes, reverse osmosis, ionic exchange and active carbon based adsorption. All of these processes have been employed and have flourished in reducing an impressive percentage of incomplete metal removal from the wastewater, but the adsorption method stands out to be one of the most versatile methods due to its easy operation, flexibility, high efficiency for metal sorption, recovery of heavy metal contaminants and reuse of the adsorbent [2]. However, the removal of heavy metals with traditional adsorbents like activated carbon is ineffective at low concentrations of heavy metals and its use is partial owing to the expense of activated carbon [3]. Furthermore, nanomaterial based adsorbents have been developed recently; their practical applications in treating wastewater are limited by their complex synthesis procedure and difficulty to separate [4]. Currently, biosorption process has gained momentum for utilizing low-cost biological materials known as the biosorbents with efficient binding capabilities towards different heavy metal ions. Such type of alternative biosorbents with cost-effectiveness is the requirement of the hour towards implementation of the process in commercial scale.

Biosorptive removal of heavy metal from wastewater has progressed significantly and is suitable for protection of the environment and human health. Still, the process has few drawbacks preventing it from achieving a good status at commercial levels. These include the lower pH dependency of the biomaterials and their slow metal removal rate compared to the chemical processes. Thus, there is a need for searching new superior biomaterials capable of eliminating metal ions more fast at a pH value closer to the actual solution pH (>pH 5.5). Further, natural biomaterials are generally selective for specific metal ions, thus for multi-metal system selection of different efficient biosorbents would be required while optimum conditions for their removals might be different from each other. Thus, use of complex biosorbent having high capacity for removal of multi metal ions need to be employed for large scale applications. One of the real challenges in the field of biosorption is to identify the mechanism that governs the metal uptake by biosorbent. Finally, the fate or consequences of the biosorbent after the biosorption process is often ignored which needs to be addressed with an environmentally safe perspective. In this aspect, recovery of the metal from the loaded biosorbent and simultaneous regeneration of the same is an important issue. Even if the biosorbent can be effectively reused over several cycles, ultimate disposal of the metal loaded spent biomass is essential to be focused considering the environmentally safe perspectives. The conventional responses to the disposal of these materials involve storage, landfill disposal or incineration which in turn again pollutes the environment. Landfill option cannot be suitable because of the possibility of contamination of ground water by leaching of heavy metals. Again, the biomass burning process is being criticized worldwide because it causes air pollution by generating hazardous volatiles and ash with high concentration of the desired metals [2].

Recreation of waste from landfill to favour reuse or recycling options and towards the development of marketable products is of high economic and/or ecologic interest. Currently few innovative suggestions have been reported in research articles for management of hazardous industrial waste sludge as ecofriendly, harmless and productive approach. The conversion of industrial sludge and/or sludge ash into useful materials including bricks, tile, concrete and cement like materials, light weight artificial aggregates, etc. can resolve disposal problems and reduce the solid waste content [5,6]. It also shows the way for fixation of toxic metals, oxidization of organic matter and destroying pathogens in the fired matrix. However, Toxic characteristic leaching procedure (TCLP) tests on brick or tile demonstrated unpredictable metal leaching for longer time periods [5].

To solve this issue, the present investigation was designed for immobilization of heavy metals waste in a glass matrix, which is considered as an appropriate option preventing the further risk of the environmental contamination. Glasses are the safer way for such inertization because they exhibit high mechanical, chemical and thermal resistance, high corrosion stability and very slow dissolution rates in water. They enable homogeneous incorporation of various elements in their disordered structures and demonstrate good tolerance due to the changes in inherent composition of the metal loaded wastes. Glasses have been explored for vitrification of nuclear waste due to its simple production technology adapted from glass manufacturing industry, reduced volume of resulting waste form and high tolerance to radiation damage [7]. Among various types, phosphate based glasses are oxide type glass having various physical, chemical and optical properties for specific technological applications. They are comparatively easy to prepare and have wide range of compositional possibility that can accommodate large concentrations of active ions, as well as, transition metal ions. The phosphate glass preparations are preferred in comparison with silicate glass due to its relatively low melting temperature, glass transition and high thermal expansion coefficient [8].

Exploitation of diverse biosorbents for removal of single metal ion has been chiefly reported in the literature [9]. However, single toxic metallic species rarely occur in natural water or wastewater, rather the existence of multiple metal ions frequently causes an interactive effect. However, insufficient attention seems to have been given to this problem. Further, only few scientific literatures reported about the biosorption mechanism governed in the metal uptake by biomaterials [10]. The illumination of biosorption mechanism and long term solution for safe disposal of the generated metal loaded waste is necessary to enable the technology to be developed.

In the present study tannery sludge was used as a biomaterial for the removal of heavy metal ions due to its low cost and accessibility [11]. It is composed of both live and dead microbial fractions as natural complex biosorbent with large number of chemical functional groups at the cell wall of biomasses that could show higher and faster sequestration rate of metal ions. The objective was to establish adsorption characteristics both in single and multi metal removal system, mechanism studies, actual industrial effluent treatment and inertization of the generated hazardous waste. Different experimental approaches involving the influence of various environmental parameters such as the pH, biosorbent