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Predictive approach for simultaneous biosorption and bioaccumulation of arsenic by *Corynebacterium glutamicum* MTCC 2745 biofilm supported on NL/$MnFe_2O_4$ composite

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ABSTRACT

The potential use of *Corynebacterium glutamicum* MTCC 2745 biofilm supported on NL/$MnFe_2O_4$ composite for eliminating both As(III) and As(V) from synthetic wastewater was inspected in a batch assay. Effects of operating parameters like pH, biosorbent dose, contact time, temperature and initial adsorbate concentration onto the removal efficiency was investigated. Minimum contact time to achieve equilibrium is 260 min at pH 7.0 at 30 °C temperature for both ions. Existence of functional groups onto the surface of biosorbent attached with biofilm that may interact with the As(III) and As(V) ions was proved by FT–IT, to estimate the applicability of this system for the elimination of those ions. To determine the most suitable correlation for the equilibrium curves employing the method of the nonlinear regression for curve fitting analysis, isotherm studies were carried out for As(III) and As(V) utilizing 30 isotherm models. The pattern of biosorption/bioaccumulation fitted well with Vieth and Sladek isotherm model for As(III) and Brouers–Sotolongo and Fritz–Schlunder-V isotherm models for As(V). D–R isotherm studies indicated that ion-exchange might play a prominent role. Desorption study was also performed with different concentrations of NaOH solution.

1. Introduction

Increased human activities as well as industrialization introduce unusual toxic elements into the environment, responsible to disturb the natural biogeochemical cycles [1] in the environment. Arsenic (As) is a naturally occurring metalloid chemical element, being the 20th most abundant element in the Earth's crust [2]. Global reports of pollution of natural water (ground and surface water) with arsenic have become a severe public health-related concern [3,4]. The natural phenomenon such as volcanic activity and weathering of rocks and many anthropogenic activities for gold mining, smelting, use of arsenical composed pesticides, fertilizers, herbicides and petroleum refining are responsible for the involvement of this poison into soil and natural water [5,6].

Copper smelting causes a huge volume of wastewater having large amounts of inorganic compounds for example heavy metals like lead, copper, zinc, iron, cadmium and bismuth etc. and highly carcinogenic metalloid like arsenic species (approximately 1979 mg/L), poses a severe threat towards man and the flora and fauna of our ecosystem contaminating the natural water tables (ground water and surface water) in the vicinity [7]. With the aim of maintaining a good quality of fresh water resources, this wastewater must be treated so that the water can be reverted to the ecosystems.

Its long term exposure causes various severe health problems such as black foot disease, respiratory problems, hyperkeratosis, and also results in various type of cancer of bladder, lung, kidney, skin and liver [2]. On the basis of study of the fatal effect of arsenic onto the human body, in drinking water the maximum contaminant level (MCL) of arsenic has been revised to 10 μg/L from 50 μg/L by the World Health Organization (WHO) in 1993 [8] and the European Commission in 2003 [9].

Arsenic can exist in the environment in many oxidation states (−3, 0, +3 and +5), however in natural water (ground and surface water) is commonly present in inorganic form as oxyanions of arsenic viz. As(III) and As(V). As(III) is more poisonous, more mobile and more problematic to be eliminated from water compared to As(V) [10]. Various physico-chemical techniques have been developed and applied for the elimination of arsenic [5,4,7]. However these high technology methods have noteworthy difficulties,

Abbreviation: MNL, NL/MnFe2O4 composite.

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Nomenclature

C_0	Initial concentration of arsenic in the solution (mg/L)
C_e	Equilibrium concentration of arsenic in the solution (mg/L)
q_e	Adsorption capacity or amount of arsenic adsorbed onto the surface of adsorbent at equilibrium (mg/g)
R_d	Distribution coefficient
R_e	Removal efficiency

including necessities for costly monitoring systems and equipment, incomplete removal of metals, high operating cost, high energy or reagent necessities and production of toxic sludge or other waste products that need discarding. New technologies are essential that can decrease concentrations of heavy metal to environmentally tolerable limits at reasonable prices [11]. Current expansion in biotechnology has recognized numerous probable approaches of remediation for example bioaccumulation or biosorption employing microorganisms like algae, fungi and bacteria [12].

Metals uptake by biomass can occur dynamically, via a passive and generally fast (several minutes) metabolism-independent process termed biosorption or via a metabolic activity dependent process termed bioaccumulation [13]. Bioaccumulation and biosorption occurs on cellular membrane by various processes with biological activity and without biological activity, respectively.

On the basis of the capability of certain biological materials for accumulating and finally for transforming molecules from wastewater by physico-chemical or metabolic reactions, the expansion of a robust, extremely modest method, with high efficiency and performance is intensely suggested. This method comprises a biosorption stage afterward a bioaccumulation stage, dependent on the microorganism capability for accumulating contaminants. The key benefits of this kind of system are the low operating cost, reusability of biomaterial, better selectivity for particular contaminants and no generation of secondary products which can be poisonous [14]. The use of microorganism for biosorption of arsenic ions from water is an enormously effective process, due to which it is becoming widespread day by day. Podder and Majumder [15,24] examined the potential of living cells of *Bacillus arsenicus* MTCC 4380 to biosorb both As(III) and As(V) in batch experimentations targeting the treatment of wastewater with high concentrations.

Bacteria devote maximum of their natural presence to grow as a biofilm. It is probable that occurrence of an appropriate substrate for attachment is all that is essential for generating biofilm formation [16]. The usage of less expensive waste biomass, the low cost of immobilization or formation of biofilm supported on the adsorbent and the probability of biomass regeneration are some of the utmost significant key factors that should be deliberated in the application of simultaneous biosorption and bioaccumulation (SBB) in the elimination of toxic metals from natural water or wastewater [17].

Corrynebacterium glutamicum MTCC 2745 species is of specific attention due to its high capability for abatement biologically. Bacteria can depollute arsenic wastewater, by accumulation outside the cells and/or biosorption of the ion on their surface [18] as was defined earlier for *Escherichia coli* [19] and *Ralstonia eutropha* [20]. *C. glutamicum* MTCC 2745 does not have an outer membrane, it contains a typical cell-surface S-layer formed by a protein encoded by *cspB* [21].

The Neem tree (*Azadirachta indica*) of the family Meliaceae is inherent in India and nearby countries for more than 2000 years and was amended for its growth in Brazil a few years earlier. Its significance has been famous by the US National Academy of Sciences which issued a report in 1992 named "Neem—a tree for solving global problems" [22]. It was on this basis that this effortlessly obtainable agricultural leaf was examined for its potential in treating industrial effluents including these metal ions.

Definitely biosorbents are significantly effective for scavenging heavy metals from aqueous phase. So the major objective of the present research was the designing of an efficient metal ion removal system mediated by immobilized bacterial cells. The removal system of metal ion designed in the present investigation was termed as simultaneous biosorption and bioaccumulation (SBB) system. For effective removal of toxic metal ions, the biomass needs to be immobilized to increase the mechanical strength and resistance to the various chemical constituents of aqueous waste [23]. Due to practical difficulties in solid–liquid separation, the free biomass are also immobilized on the support. Immobilized biomass also shows better potential in packed/fluidized bed reactors and continuous stirred tank reactors due to minimal clogging under continuous flow conditions as well as effective biosorbent regeneration and metal recovery [23]. Arsenic removal efficiency of bacteria improves when it is immobilized on a solid support like GAC [5]. Podder and Majumder [15,24] reported the bio-removal of arsenic from wastewater by using *B. arsenicus* MTCC 4380 and Neem leaves/$MnFe_2O_4$ composite in a batch reactor. They observed simultaneous biosorption bioaccumulation (SBB) when Neem leaves/$MnFe_2O_4$ composite was used as supporting media for bacterial immobilization. Podder and Majumder [25] also reported the bio-removal of arsenic from wastewater by using *C. glutamicum MTCC* 2745 and Neem leaves/$MnFe_2O_4$ composite. In the present investigation, NL/$MnFe_2O_4$ composite was utilized as carrier for immobilization of bacteria *C. glutamicum* MTCC 2745 owing to its easy obtainability and cost efficiency. The ideal biofilm will be one that preserves bacteria via entrapment, though is open sufficient not to smother the NL/$MnFe_2O_4$ surface (i.e. so that it remains accessible for biosorption/bioaccumulation of organic residues etc.).

The objective of the current research was divided into two parts. First part of the study were 1) to prepare NL/$MnFe_2O_4$ composite which was composed of acid treated neem leaves (NL) and $MnFe_2O_4$ via a facile coprecipitation method, 2) to determine the existence of functional groups in the biomass and to explain the mechanism of As(III) and As(V) scavenging by immobilized bacterial cells using FTIR and SEM-EDX and 3) to inspect the biosorption/bioaccumulation behaviour of immobilized bacterial cells for the scavenging of As(III) or As(V) from synthetically prepared copper smelting wastewater by optimizing initial pH of the solution, biosorbent dose, contact time, temperature and initial arsenic concentration

The second part of the current study was to study thirty adsorption isotherms for both As(III) and As(V) on the surface of immobilized bacterial cells (SBB) to inspect their ability for modelling the biosorption/bioaccumulation equilibrium data.

2. Materials and methods

2.1. Materials

Neem leaves were collected from the institute campus of Indian Institute of Technology, Roorkee, India. The stock solutions of As(III) (1000 mg/L) and As(V) (1000 mg/L) were prepared by dissolving sodium arsenite ($NaAsO_2$) and sodium arsenate (Na_2HAsO_4, $7H_2O$), purchased from Himedia Laboratories Pvt., Ltd., Mumbai India, in double distilled water, respectively. All other necessary chemicals used in the experiments, were of analytical reagent grade and were purchased from Himedia Laboratories Pvt., Ltd., Mumbai India.