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Biofilter column for removal of divalent copper from aqueous solutions: Performance evaluation and kinetic modeling

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ABSTRACT

In recent years, the biofiltration technique has gained significant importance for the removal of toxic organic compounds. However, very limited studies on biofiltration were carried out for the removal of divalent copper [Cu(II)] from aqueous solution using indigenous packing material. There are no reports in the literature that deal with the performance evaluation and kinetic modeling of the biofilter column for the removal of Cu(II). In the present study, a lab- scale biofilter column was fabricated and packed with a mixture of compost and coal as a packing material. The seeding of the column was done using an indigenous bacterial strain *Acinetobacter guillouiae*. The removal of divalent copper [Cu(II)] was investigated in this column for a period of 55 days. The maximum removal efficiency of 97.5% was achieved during phase II for Cu(II) inlet concentration of 20 mg L^{-1}. During shock loading, maximum removal efficiency obtained was 87% for initial Cu(II) concentration 28.5–30 mg L^{-1}. The Michaelis–Menten kinetic constants obtained were 0.2 mg L^{-1} min^{-1} and 13.03 mg L^{-1}. It was found that the Ottengraf model with zero-order diffusion-limitation fits the experimental data quite well for phase II, III and V.

1. Introduction

Fast industrialization worldwide is causing water, soil and air pollution. Most of these industries are discharging toxic heavy metals which are non-biodegradable. These metals are transported through water bodies and get precipitated in the soil matrix. A great amount of various toxic metals are released every day of which divalent copper [Cu (II)] is considered to be highly toxic to the environment and human beings. Cu(II) is an essential element to living organisms at trace level but intake of excessive copper may lead to capillary damage, renal failure, stomach ulcer, damage of central nervous system, Wilson's disease etc. [1]. Several treatment methods have been reported for the removal of copper from wastewater. These methods include electrochemical process, membrane filtration, chemical precipitation, ion exchange and adsorption [2,3]. However, all these methods have certain disadvantages. Most of these methods require high capital and operating costs, high energy requirements and also create toxic sludge which needs to be further treated before releasing to the environment [4]. Bioremediation, which uses living micro-organisms has gained a significant attention for the removal of Cu(II) from aqueous solution [5,6]. Cu(II) ions get entrapped in the cellular structure. It can also be transported inside the cell through the metabolic cycle and may react with cell proteins to form a Cu–protein complex.

Biofiltration uses the bioremediation principle in which microorganisms are attached to a relatively inert packing material to remove the pollutants present in the wastewater stream. The packing medium plays an important role for the overall effectiveness of the biofilter operation [7]. In a biofiltration operation, removal of pollutants takes place through various steps such as attachment of microorganisms on the surface of filter medium, formation of a thin of biofilm, progressive growth of the microorganisms and decay & detachment of microorganisms [8,9]. Biofiltration was first successfully used as a trickling filter for the removal of various heavy metal contaminants from industrial wastewater [10]. In recent years, biofiltration has widely been used for the treatment of various volatile organic compounds [9,11–15]. Its application in the area of heavy metals removal is scarce. Moreover, this technology is not well established in the field of heavy metal removal. Søgaard et al. [16] studied the removal of iron in a sand filter using *Gallionella ferruginea* in biotic condition. Removal of iron was also carried out by maintaining abiotic conditions. They have compared the rate of iron precipitation in both conditions and reported that biotic iron precipitation is 60 times faster than abiotic precipitation. Some more studies were reported for the removal of

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heavy metal such as Zn [17], As [18], Cd [18], Cr [19,20] and Cu [6,21]. It is evident that significant amount of selective heavy metals can be removed using biolfiltration. In biofiltration, the effective removal of heavy metals mainly depends on the selection of microbial culture and packing materials. Different packing materials used in earlier studies were coal, peat, compost, sand and soil. Most of these studies were carried out using a single packing material which caused severe operational problem such as development of back pressure in the column hydrodynamics, aging effect due to microbial mineralization and poor attachments of biolfilm on the surface of packing. Moreover, these studies were not focused on the effective use of packing materials in combination which may prove to be cheaper and effective for the successful operation of biolfiltration. Raghuvanshi and Babu showed that a hybrid bed system consisting of coal and matured compost gives better removal of methyl ethyl ketone using a mixed consortium of microorganisms [14].

In earlier studies, kinetic modeling of biolfiltration of heavy metals were not explored which is necessary in designing and understanding the behavior of the column during the continuous operation. The present work deals with the removal of Cu(II) from aqueous solution using biofiltration. A mixture of coal and matured compost was used as packing material as reported in an earlier study [14]. The seeding of the column was carried out using an indigenous bacterial strain, *Acinetobacter guillouiae*, isolated from the activated sludge of a Sewage Treatment Plant (Pilani, India). The performance of the column was evaluated for a period of 55 days in terms of removal efficiency and elimination capacity. A study was carried out for inlet concentrations of Cu(II) in the range of 10–50 mg L^{-1} and flow rates of aqueous Cu(II) solution in the range of 5–40 mL min^{-1}. A study was also conducted to check the stability of the biofilter column for Cu(II) removal under shock loading conditions for a period of 14 days immediately after the 55 days of biolfilter operation. Kinetic aspects of bioremediation process during the biofiltration was also understood by fitting the experimental data with the Michaelis–Menten kinetic model. The Ottengraf–Van Den Oever model with zero-order diffusion limitation was validated using the experimental data.

2. Experimental methods

2.1. Media preparation

A 1000 mg L^{-1} stock solution of Cu(II) was prepared by dissolving 3.928 g of copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) in distilled water and the solution volume was made up to 1 L. A similar procedure was followed to prepare a 1000 mg L^{-1} stock solution of Cd(II) by weighing 1.8274 g of cadmium chloride mono hydrate ($CdCl_2$, H_2O). It was used to check the efficacy of isolated bacterial strain in Cd(II) removal. These stock solutions were further used to prepare different concentrations of Cu(II) and Cd(II) solutions (10, 20, 30 and 50 mg L^{-1}). The minimal salt media (MSM) consisted of the following mineral salts in specific amounts: K_2HPO_4 – 0.8, KH_2PO_4 – 0.2, $CaSO_4{\cdot}2H_2O$ – 0.05, $MgSO_4{\cdot}7H_2O$ – 0.5, $(NH_4)_2SO_4$ – 1.0 and $FeSO_4$ – 0.01 (in g L^{-1}). All these salts were weighed and added in 1 L of distilled water. Glucose was used as carbon source in the present study. A 10,000 mg L^{-1} stock glucose solution was prepared by dissolving 10 g of D-glucose in 1000 mL distilled water. The nutrient agar media used in isolation and cultivation of bacteria consisted of peptone 5 g, beef extract 1.5 g, yeast extract 1.5 g, agar 15 g and sodium chloride 5 g in 1 L distilled water [22]. All the reagents and salts used were of analytical grade and procured from Merck, India. 1 M HCl or 1 M NaOH was used to adjust the pH of all media at 7.0 ± 0.2. A 100 mL of 0.8% of NaCl stock solution was prepared by dissolving 0.8 g of NaCl in 99.2 g of distilled water and then it was sterilized. This solution was used to isolate the microorganisms from the bioflim formed over the packing material. All media were made contamination free by sterilizing in a Vertical Autoclave (MSW-101, Macro Scientific Works, India) at 15 kPa and 120 °C for 30 min. Microbial samples were incubated at 37 °C and at 100 rpm in a biological oxygen demand (BOD) incubator and shaker (MSW-132, Macro Scientific Works, India).

2.2. Enrichment of Cu(II) tolerant bacterial strain

Activated sludge was collected from the Sewage Treatment Plant of Pilani, India. A similar procedure was followed to pretreat the activated sludge and enrich the aerobic mixed culture as reported in an earlier study [23]. Enriched microbial culture was then used for isolation of Cu(II) tolerant bacteria. Repeated serial dilutions followed by the streak plate method were employed to isolate the Cu(II) tolerant bacteria [23]. Single identical colonies were separated based on their morphology and streaked on nutrient agar slants using an inoculating needle. The isolated microbial strain was identified as *A. guillouiae* (GenBank accession number: HQ538658.1). The strain was incubated and then stored at 4 °C until used for biofiltration experimentation.

Different microorganisms have diverse levels of metal intake capacity and metal specificity for certain metals. In a mixed culture, microorganisms compete with each other to remediate the metals from aqueous solution which may significantly reduce the overall performance of the biofilter column. Due to this reason, single bacterial strain *A. guillouiae* was used in the present study for biofiltration experimentation.

2.3. Cd(II) removal efficiency of isolated bacterial strain

To evaluate the removal of other metal ions using the isolated bacterial strain, a separate batch study was conducted. In this study, several sets of 250 mL conical flasks containing 100 mL sterilized MSM supplemented with Cd(II) (initial concentrations: 10, 20, 30 and 50 mg L^{-1}) were used. Sample was inoculated with a 1% (v/v) of suspension of *A. guillouiae* and then incubated at 37 °C and 100 rpm. Flasks were withdrawn at regular intervals (2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 28 and 32 h) and the samples were analyzed for final Cd(II) concentration.

2.4. Development of the biofilter column and its operation

In a biofilter column, a mixture of matured compost and coal (1:1 w/w) was used as packing material. The coal was procured from the local market of Pilani, India. It was crushed and sieved through 8–10 mm mesh screen. The final coal size obtained was 2.36 mm. The coal was washed with distilled water to remove impurities. It was kept in a hot air oven (MSW-211, Macro Scientific Works, India) at 100 °C for 1 day to remove moisture present in it. The matured compost was obtained from The Dairy, Birla Education Trust (Pilani, India). It was derived from cow dung. The coal and compost was then mixed with 200 mL of bacterial strain as reported in an earlier study [14].

The biofilter was made using perspex tube of 5 cm inner diameter and 1 m length (Fig. 1). The biofilter column was packed with packing material and it was supported on two stainless steel meshes fixed at the top and bottom of the column, as shown in Fig. 1.

The packing height was maintained at 70 cm. The entire biofilter set-up was kept inside a laminar air flow closure to maintain the aseptic condition throughout the entire experimentation. 300 mL of bacterial strain was then transferred to the packed column three times in order to ensure proper mixing of bacterial strain with the packing material [14] . The leachate collected at the bottom during