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Treatment of water containing heavy metals using a novel approach of immobilized modified sludge biomass based adsorbents

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The biosorption potential of modified sludge biomass (MSB) immobilized by various mechanisms was investigated for removal of Cu(II) and Cr(VI) metals. The sorption efficiency (mg g^{-1}) decreased in the order Polyvinylalcohol-carboxymethylcellulose sodium salt-activated carbon (PVA-CMC-AC) > Polyvinyl alcohol-carboxymethylcellulose sodium salt (PVA-CMC) > Polyvinylalcohol (PVA) > calcium alginate (CA) under the optimized operating conditions as pH of 5.0, metal concentration of 0.1 g L^{-1}, adsorbent loading as 0.1 g MSB/100 mL and treatment time of 85 min as established in the work. The equilibrium data fitted well with Langmuir isotherm model and pseudo first order kinetic model. 20% $CaCl_2$ was established as best eluting agent and the regenerated adsorbent can be used in 5 cycles with marginally reduced efficacy.

1. Introduction

Water pollution due to the presence of heavy metals is a major environmental concern. Presence of metals may originate from several industries and its occurrence has become a major risk to plant, animal and human life due to the bioaccumulation tendency and toxicity of heavy metals. It is imperative that proper treatment techniques are developed for effective removal of heavy metals from municipal and industrial effluents before discharge as the existing conventional methods offer limitations both in terms of efficacy and economics [1]. Use of biological materials as bioadsorbent for the removal of heavy metals has received significant attention in the recent years because of the good performance, eco-friendly nature and low cost for the adsorbent [2]. Microbial biomass, both metabolically inactive or dead and living are able to bind and accumulate metal species and can be used as biosorbents in addition to the more commonly used sustainable materials derived from biomass. The dead biomass offer more advantages as it can be obtained as by-products from fermentation or biological oxidation, no nutrient supplementation is required and these can be easily regenerated [3,4]. The present work has focused on the use of such dead biomass obtained as a residue during the treatment of organic contaminants using the modified activated sludge [5]. The model contaminants selected in the present work are Cu(II) and Cr(VI) based on the significant importance in the industrial activities. Cu ions are non-degradable and persistent leading to serious environmental problems, which makes the effective removal from the wastewater of primary importance [4]. Cr (VI) is also of a great concern because of its toxicity to humans, animals, plants and microorganisms [6]. Cr(VI) has also shown some carcinogenic effects. The present work has concentrated on developing an efficient process for the removal of these two metal ions based on the use of modified sludge biomass (MSB) as adsorbent.

Immobilization of biosorbents is very essential for the industrial application because large volumes are required to be treated [7] and it becomes imperative that the biosorbent is easily separated from wastewater to be available for reuse. Use of porous media is an important requirement for the attachment of biomass to significantly enhance the efficacy of separation. Polymeric media would be a suitable material for these purposes because of the offered large area and production at low cost with precision and repeatability. Immobilization of biomass can be performed using different entrapment materials such as alginates, polyacrylamide, polysulfone, polyvinyl formal, polyacrylamide, cellulose, polyvinyl alcohol (PVA) and carboxymethylcellulose sodium salt (CMC) [8–13]. CMC is a biodegradable, naturally present polymer with large number of functional groups being present on the surface [14–16], which makes CMC a good candidate for immobilization. Al-Hakawati and Banks [7] studied the application of different polymers such as polyvinyl formal, polysulfone, polyurethane, alginate, polyacrylamide, k-carrageenan and polyethyleneimine

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(PEI) for entrapment of biomass and reported that immobilization using different polymer medium at high rate was difficult due to agglomeration of biomass. In addition, microscopic examination of the polymer/biomass entrapment showed little sign of a porous matrix hindering the possible rapid diffusion of metal ions to the biomass binding sites. Thus it is important to properly select the polymer support as well as control the synthesis conditions so that the desired characteristics are obtained. Entrapment of biomass in polyvinyl alcohol (PVA) and cellulosic material could be effective also giving enhanced mechanical strength and the biosorption characteristics could be superior leading to higher removal extents of the heavy metals from wastewater and soil [15]. Additional benefits include low material cost, rapid formation of beads by simple procedure and easy application in fluidized bed reactors due to higher elasticity and high strength characteristics of PVA beads [11]. Earlier studies have mostly concentrated on pretreatments or modifications in the biomass with an objective of obtaining enhanced surface area which may enhance the sorption capacity for the removal of pollutants from aqueous solution [17]. Though different materials have been used for immobilization of different biomass, not much information has been reported on the use of a non-living modified sludge biomass and the comparison of the different polymeric media as support for the immobilization. Based on this analysis, different approaches of immobilization were applied for the attachment of MSB and the efficacy was investigated for metal removal in terms of the removal efficiency and the equilibrium isotherm as well as kinetic parameters. The effect of different operating parameters (i.e., pH, adsorbent dose, contact time and initial concentration) has also been investigated. The adsorption isotherm was evaluated by fitting the experimental data to the two parameter models such as Langmuir, Freundlich and Dubinin–Radushkevich (D–R) and three parameter models such as Redlich–Peterson (R–P) and Radke–Prausnitz. The experimental data was accurately interpreted to determine the isotherm parameters by least square fitting analysis method. Similarly, the kinetics of adsorption was investigated using pseudo-first-order and pseudo-second-order kinetic equations as well as the intra-particle diffusion model.

2. Materials and methods

2.1. Model metal system and analysis

The heavy metals studied in the present work were copper [Cu (II)] and chromium [Cr(VI)]. The stock solutions of Cu and Cr (initial concentration of 1000 ppm) were prepared by dissolving copper sulfate and potassium dichromate [obtained from S.D. Fine Chemical Pvt. Ltd.] in deionized water respectively.

After the studies for adsorption, the biomass contained solutions were filtered using Whatman filter papers (No. 41). The concentration of Cu(II) in the filtered solution was determined using atomic absorption spectrophotometer (Perkin Elmer 2380) according to the guidelines of ASTM D 1688. Concentration of Cr(VI) was estimated using the 1,5-diphenylcarbazide method using a UV–visible spectrophotometer (Perkin–Elmer, Lamda-35) operated at 540 nm according to the ASTM D 1687 standard test method [18].

2.2. Modified sludge biomass (MSB) adsorbent

The modified sludge biomass (MSB) was obtained as a residue from the biological oxidation of different organic compounds using modified activated sludge [5]. The biomass solids were filtered and dried at 60 °C for 12 h. The dried biomass was powdered in a mortar by pestle apparatus and sieved into different fractions between mesh sizes 16 and 20 which gives a particle size range of 0.85–1.15 mm. The sample of MSB biomass was examined using scanning electron microscopy (SEM) for surface analysis (SEM) (JEOL, JSM-6330 LA). MSB was also analyzed using Fourier transform infrared (FTIR) Spectrometer (FTIR-2000, Perkin–Elmer) to establish the functional groups over the absorption wavelength range of 4000–400 cm^{-1}.

2.3. Immobilization of MSB adsorbent

The prepared MSB was used in all experiments in the immobilized form using different supports designated as MSB-CA, MSB-PVA, MSB-PVA-CMC-AC and MSB-PVA-CMC. The procedure for preparation of each of these forms has now been described here.

MSB-CA was synthesized by entrapment in sodium alginate. The mixture of 2% (w/v) sodium alginate and 1 g of MSB were stirred using a magnetic stirrer. The alginate MSB slurry was introduced into 0.15 M $CaCl_2$ solution through a syringe needle (No. 18) for spherical bead formation generally observed to be in the range of 2.5–3.0 mm in diameter [19,20]. The prepared beads were preserved in the $CaCl_2$ solution for 12 h to enhance their mechanical stability. The beads were then incubated for 2 h in $CaCl_2$ rinsed with distilled water and stored at 4 °C in 50 mM $CaCl_2$ solution.

Immobilization of MSB biomass in phosphorylated PVA gel named as MSB-PVA was carried out according to method reported in the earlier work [21].

MSB-PVA-CMC-AC was synthesized by drop wise addition of the solution (50 mL volume) containing PVA (20 wt.%), CMC (2.0 wt.%), MSB (2.0 wt.%) and 0.5 g activated carbon (AC) into a solution containing saturated boric acid with 0.1 M $CaCl_2$ after adjusting the pH to 7.0. The prepared beads (2.5–3.0 mm) were stored for 10–12 h at room temperature in fresh $CaCl_2$ for crosslinking. Finally, the beads were washed with normal saline water (about three times quantity) to remove the excess Ca^{2+} ions and free biomass and stored at 4 °C for subsequent use. Concentration of PVA and AC for synthesis of MSB-PVA-CMC-AC immobilized beads was kept constant based on the required condition of higher metallic bonding which minimize the agglomeration of metal and MSB to give higher surface area [21].

MSB-PVA-CMC beads were prepared by mixing PVA (20 wt.%, 50 mL) and CMC (4.0%, 50 mL) with 2.0 g MSB biomass as per the similar method described for the case of MSB-PVA-CMC-AC. The immobilized biomass obtained on PVA-CMC composite was tagged as MSB-PVA-CMC. The prepared and dried immobilized MSB beads in different polymer systems by different immobilization techniques have been shown in Fig. 1.

2.4. Adsorption methodology

2.4.1. Batch adsorption studies

The efficacy of immobilized forms of MSB in different polymer systems for the sorption of Cu(II) and Cr(VI) has been investigated by conducting several experiments in batch mode. All experiments were carried out in 250 mL conical flasks placed on an orbital shaker (Remi Orbital shaking incubator) at 200 rpm over a time period of 120 min [7]. Samples (5 mL) were withdrawn at regular time intervals and centrifuged at 12,000 rpm for 5 min. The supernatant was examined for Cu(II) and Cr(VI) concentrations using the methods described earlier.

The effect of pH was investigated by conducting the experiments at constant Cu(II) and Cr(VI) concentration as 0.1 g L^{-1} using 0.1 g of MSB biosorbent (1.0 g of dried immobilized MSB bead) in 100 mL solution (giving a adsorbent loading of 1 g L^{-1}) for a fixed treatment time as 120 min with varying pH over the range 2.0–6.5. The pH value of the solution was adjusted using 1 N HCl or 1 N NaOH as per the requirement. The effect of contact time on the adsorption was also investigated over a time range of