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The removal of heavy metals in a packed bed column using immobilized cassava peel waste biomass

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ABSTRACT

Several studies on the removal of heavy metals in batch systems using cassava waste biomass have been reported in literature. However, for practical and large scale operations, packed bed columns are preferred. This study investigated the biosorption of heavy metals (Cr^{3+}, Co^{2+} and V^{3+}) onto immobilized cassava peel waste in a packed bed column. Experiments were conducted with 100 mg/L of combined metal ion solutions under different flow rates (0.83–1.61 mL/s) and bed depths (5–15 cm). The dynamic behaviour of the process was described in terms of the breakthrough curves. The results showed that the removal efficiency was favoured by low flow rate and high bed depth. Biosorption efficiency was found to increase in the order $V^{3+} > Cr^{3+} > Co^{2+}$ for all conditions tested. Amongst the two well-established column models tested, the bed depth service time (BDST) model with biosorption capacities of 99.6, 116.2 and 132.8 mg/L for Co^{2+}, Cr^{3+} and V^{3+}, respectively, fitted experimental data very well. The column was regenerated and reused six times consecutively without significant loss in biosorbent capacity signifying its appropriateness for commercial application.

1. Introduction

The presence of heavy metals in water and wastewater effluents is one of the greatest challenges in our time. This is because a variety of physiological and neurological damage to the human body are associated with heavy metal exposure [1]. As a result tough regulatory laws that restrict levels of heavy metals present in water or wastewater have been imposed by several nations in the past decades. Therefore, in order to decrease the levels of heavy metals in the environment, it is necessary to treat wastewaters before discharge [2]. At the moment, a wide range of physical and chemical techniques are available for removal of heavy metals [3]. However, these traditional water and wastewater treatment processes have shown to be prohibitively expensive and ineffective for very low metal concentrations [4–8]. Therefore, the need to find effective and economical alternative techniques for removal of heavy metals is taken as a priority in the water and wastewater treatment industry. One such alternative technique that has attracted a lot of attention in recent years because of its competitiveness, effectiveness and low cost is biosorption [3,6,8–15]. Furthermore, biosorption exhibits several other advantages, such as high selectivity and low energy consumption [16]. In recent past, a wide range of biosorbents such as rice husks [17], neem saw dust [8], beer yeast [18], green algae [19] and fly ash [20] have been investigated. More recently [6], we investigated the removal of some heavy metals from waste effluents using cassava peel waste in a batch system.

The biosorption capacity of the cassava peel waste [6] and many other biosorbents obtained from batch equilibrium experiments is useful in providing fundamental information about the effectiveness of metal-biosorbent system [21]. However, data obtained from batch systems may not be applied directly to most treatment systems (such as column operations) where contact time is not sufficient for the attainment of the equilibrium [8,21–23]. Furthermore, batch systems are usually limited to the treatment of small quantities of wastewater [21]. Therefore, for practical and large scale operations, a packed column is preferred to a batch system [8,19,22]. This is because a packed column makes the best use of the concentration difference known to be the driving force for heavy metal biosorption. This allows for more efficient utilization of biosorbent capacity and also results in better quality of the effluent [8,22,24]. Hence, a column packed with immobilized cassava peel waste pellets was used in our study. In such systems,

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the concentration profiles in the liquid and biosorbent phases vary in both space and time [19,25]. This makes the design and optimization of a packed bed difficult to perform without a quantitative modelling approach [19,25].

Models have an important role in technology transfer from laboratory-scale to industrial-scale [24]. Appropriate models can help to analyze and explain experimental data, identify process mechanisms, predict answers to changing operational conditions and optimize processes [24,26]. From the perspectives of process modelling, the dynamic behaviour of a packed column is described in terms of a breakthrough curve [8,19,25]. A breakthrough curve, which is S-shaped, is a plot of effluent solute concentration versus time. Breakthrough is the point on the S-shaped curve at which the effluent solute concentration reaches its maximum allowable value [8,22]. On the other hand, the point where the effluent solute concentration reaches 95% of the influent concentration is called the point of column exhaustion [8,22,27].

The shapes of breakthrough curves depend on the nature of the wastewater being treated. If there is only a single adsorbable component in wastewater, the adsorption will be short and the breakthrough curve will be steep [8,22]. If there is a mixture of components having different adsorption capabilities, the sorption zone will be deep and the breakthrough will be flatter. Residence time is the major design parameter for the adsorption systems. The optimum residence time determines the size of the adsorbing column and amount of adsorbent.

As stated earlier, the potential of utilising cassava peel waste as a biosorbent for the removal of some heavy metals from aqueous solutions was investigated in our previous study using a batch process [6]. Although the use of cassava biomass had shown much potential in the development of several bioprocesses in the past, there were still some questions that required answers. Therefore, some of the parameters tested in our previous study [6] included biomass modification, and its reusability. Furthermore, the choice of cassava peel waste was also made from an economic standpoint. Since cassava peel waste has no economic value its conversion into an effective biosorbent is expected to increase its market value and ultimately economically benefit the millions of cassava producers [6]. Therefore, the aim of the current study was to use immobilized cassava peel waste pellets as a biosorbent for the removal of heavy metal ions from water and wastewater in a column mode.

2. Materials and methods

2.1. Preparation of heavy metal solutions

All chemicals used were of analytical grade and were obtained from Merck, South Africa. Synthetic solutions (100 mg/L) with combined metal ions of Cr^{3+}, Co^{2+} and V^{3+} were prepared by dissolving required salt quantities of $Cr(NO_3)_3 \cdot 9H_2O$, $CoSO_4 \cdot 7H_2O$ and VCl_3, respectively, in distilled water according to the procedure outlined by American Public Health Association [28]. Relatively low metal ions concentrations of 100 mg/L were used so as to obtain gentle breakthrough curves [29]. It must be noted, however, that industrial effluents usually contain higher values than used in many studies [6]. In the previous study by Ndlovu et al. [6], the average optimum pH for biosorption of the heavy metals was 4.0. Therefore, the pH of influent solution was adjusted to 4.0 with a pH meter (827 Metrohm) by using 0.1 M H_2SO_4 and/or 0.1 M NaOH accordingly.

2.2. Preparation of immobilized cassava peel waste biosorbent

The preliminary preparation of cassava peel waste biomass was described in our earlier study [6]. The thiolation (a process of introducing sulfhydryl group (or thiol group), –SH) procedure of the cassava waste was done as described by Abia et al. [9]. Initially, the cellulose biomass was thoroughly washed with 0.3 M HNO_3 and was then filtered afterwards. The filtrate was discarded and the residue was washed with distilled water until a pH of 7.0 was obtained. Later, the paste obtained was air-dried.

The air-dried biomass was divided into 3 equal portions. The first portion was left untreated. The other two portions were treated with 0.5 M and 1.0 M thioglycollic acid, respectively, as follows: a 25 g portion was mixed with 250 mL of the required concentration of thioglycollic acid solution in the presence of hydroxylamine (NH_2OH). The mixture was mechanically stirred for 6 hours at 30 °C. This allowed the thiolation of the methylene hydroxyl group of the cellulose pyran ring [9]. In other words, the process led to the exchange of the hydroxyl groups by the sulfhydryl groups in the presence of hydroxylamine (NH_2OH) as follows:

$$B - CH_2OH + HSCH_2CO_2H + NH_2OH \rightarrow B - CH_2 - SH + CH_2CO_2H + HONH + H_2O \quad (1)$$

where B represents the biomass. The mixture was then allowed to settle overnight and then centrifuged at 2500 × *g* for 10 min. The supernatant was discarded and the paste was air-dried.

It must be noted, however, that although grinding of dried biomass may yield stable biosorbent particles, generally the free biomass has low mechanical strength not suitable for use in column applications [30]. Furthermore, whilst excessive hydrostatic pressures are required to generate suitable flow rates in packed columns, high pressures can disintegrate the free biomass. These problems can be avoided by the use of immobilized biomass systems [31,32]. Immobilized biomass offers many other advantages including better regeneration and reusability, high biomass loading and minimal clogging in continuous flow systems [33–36].

Therefore, in this study, immobilized cassava peel waste biomass was used. Cassava peel waste biomass was immobilized into small sized pellets by, firstly, mixing the free biomass with 250 mL distilled water and left to hydrate for 10 min at room temperature. Secondly, the slurry was mixed with equal volume of 3% (w/v) sterile sodium alginate. Finally, the sodium alginate-biomass mixture was added drop wise through a syringe into 0.2 M calcium chloride ($CaCl_2$) solution so as to get even-sized pellets. The sodium alginate–biomass mixture droplets solidified upon contact with $CaCl_2$, forming pellets and thus entrapping biosorbent particles. The pellets were allowed to harden for 30 min and were then washed with 0.9% sodium chloride (NaCl) solution to remove excess calcium ions [37]. The generated pellets had a diameter ranging from 3 to 4 mm.

2.3. Characterization tests

In order to identify the functional groups responsible for the biosorption in the immobilized cassava peel waste biomass, Fourier transform infrared (FT-IR, Bruker Tensor 27) spectroscopy analysis was carried out. Scanning electron microscopic (SEM, FEI Quanta 400F) studies were also conducted to observe the surface morphology of the biosorbent.

2.4. Packed bed column tests

The column experiments were conducted in a glass column with an inner diameter of 5 cm and height of 50 cm packed with immobilized cassava peel waste pellets. The column was packed with immobilized cassava peel waste pellets between two supporting layers of glass wool. The combined metal solution of 100 mg/L concentration at a pH of 4 was pumped upward through the column using a peristaltic pump (Watson Marlow 504S) with