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A Comprehensive Study on Adsorption Behaviour of Direct, Reactive and Acid Dyes on Crosslinked and Non-crosslinked Chitosan Beads

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Abstract

Chitosan beads demonstrate good adsorption capacity in wastewater treatment. The ease with which the chitosan beads separate from the effluent and the possibilities of sorbent regeneration have made chitosan beads a more prominent form for biosorption. However, chitosan beads form gels at pHs below 5.5, which makes them unsuitable to be employed in treatment process. Bifunctional agents are introduced to increase the integrity of the beads by crosslinking chitosan. Crosslinked chitosan beads exhibit different adsorption capacities for distinct types and categories of dyestuffs. In this study, the removal of Direct Red 80 (DR80), Reactive Yellow 25 (RY25) and Acid Blue 25 (AB25) dyes by chitosan-based beads has been investigated. Variation in pH and temperature, effect of crosslinking and encapsulation of bacteria *Lactobacillus casei* are evaluated for their influence on the adsorption behaviour. Zeta potential and structural characterization of the synthesized chitosan beads are performed. Adsorption equilibriums are achieved in about five hours. The chitosan beads are crosslinked with glutaraldehyde to avoid their dissolution at pH 2 and the beads achieve complete removal of the three dyes within one hour. Temperature increase induces a positive effect on the adsorption of DR80, but an insignificant effect on that of RY25 and negative effect on AB25. Adsorption with the crosslinked beads at pH 5.5 and 37 °C promotes the removal of RY25 and AB25 by at least two folds more than that by non-crosslinked chitosan beads, but is found to be less effective on DR80. Significant increase of DR80 adsorption is achieved by adopting the crosslinked-bacteria-encapsulated chitosan beads while the effect on AB25 and RY25 are similar when compared to blank crosslinked beads. Langmuir and Freundlich isotherms fit the experimental data and the pseudo-second order equation agrees very well with the kinetic data.

Keywords: Chitosan Beads; *Lactobacillus Casei*; Dye Adsorption; Langmuir; Freundlich

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1 Introduction

Among the 0.7 million tons of dye produced worldwide, 5-10% comes from the textile industry and is discharged into waste streams annually [1]. Most of these dyes are synthetic dyestuffs which are highly visible in water even at low concentrations. This will significantly affect photosynthesis-related activity that relies on sunlight penetration. Proper treatment of textile effluent becomes environmentally important. Direct Red 80 (DR80), Reactive Yellow 25 (RY25) and Acid Blue 25 (AB25) are anionic dyes commonly used in textile industry. They produce strong colour intensities owing to their extensive chromophores, thereby influencing hydrosphere. They all possess sulfonate groups which contribute to efficient adsorption as far as ionic interaction with adsorbent is concerned, i.e. DR80, RY25 and AB25 have six, two and one sulfonate groups respectively. Moreover, the molecular mass of these three dyes are significantly different, i.e. DR80 1373.07 $g \cdot mol^{-1}$; RY25 788.4 $g \cdot mol^{-1}$; AB25 416.38 $g \cdot mol^{-1}$. In order to investigate the influence of functional groups and molecule size on dye adsorption, these three dyes were chosen as the study model.

Conventional physical and chemical treatment techniques, including activated sludging, trickling filtering, chemical oxidation and coagulation, have been extensively studied to remove dyestuffs from water bodies [2]. However, the dyestuffs are usually recalcitrant molecules which are stable towards oxidation and resistant to biodegradation. Therefore, the sorption technique has been introduced and successfully employed for the removal of toxic dye molecules [3]. Although activated carbon is an effective sorbent in treating dye laden wastewater, the high cost and regeneration difficulties of the material make it unfavourable for commercial applications. Biosorbents, which are sorbents either as waste biomaterials or materials derived from bio-origins, have been investigated for colour removal by biosorption owing to their tonnage quantities and low cost. Some common biosorbents used for this purpose are peanut hulls [4, 5], fruit peels [6, 7] and rice husks [8, 9]. Moreover, different types of synthetic polymer are also evaluated as brilliant adsorbents, e.g. compounded polyethylene terephthalate with Boltorn H40 [10]. In particular, chitosan presents itself as an excellent biosorbent which can even achieve a higher dye removal capacity than activated carbon [11] with other beneficial terms such as natural abundance, biodegradability and low cost [12].

Chitosan, a deacetylated form of chitin, is a biopolymer of glucosamine which contains high contents of amine and hydroxyl functional groups. In acidic conditions, the amine groups of chitosan are protonated to electrostatically attract anionic dye molecules, thereby removing dye from an aqueous solution. When compared with chitosan flakes, chitosan beads demonstrate more superior adsorption capacity in wastewater treatment studies [13]. Besides that, the ease of separation of chitosan beads from effluent and the possibility of sorbent regeneration have made chitosan beads the more prominent form for biosorption. Nevertheless, chitosan beads form gels at pHs below 5.5, which makes them unsuitable to be employed in the treatment process. Bifunctional agents are introduced to increase the integrity of the beads by crosslinking the chitosan. Crosslinked chitosan beads exhibit different adsorption capacities for distinct types and categories of dyestuffs, and thus they are of interest for maintaining the integrity of the beads while maximizing their adsorption capacity.

In this study, the efficacy of the adsorption DR80, RY25 and AB25, by chitosan beads under different conditions is presented. The adsorption capacities of non-crosslinked, glutaraldehyde-crosslinked and *L. casei*-encapsulated chitosan beads are investigated. Since the adsorption capacity of anionic dyes in aqueous solutions is influenced by the pH, temperature of the bulk