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One step effective removal of Congo Red in chitosan nanoparticles by encapsulation

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ABSTRACT

Chitosan nanoparticles (CNPs) were prepared with ionotropic gelation between chitosan and tripolyphosphate for the removal of Congo Red. The production of chitosan nanoparticles and the dye removal process was carried out in one-step. The removal efficiency of Congo Red by encapsulation within chitosan from the aqueous solution and its storage stability are examined at different pH values. The influence of some parameters such as the initial dye concentration, pH value of the dye solution, electrolyte concentration, tripolyphosphate concentration, mixing time and speed on the encapsulation is examined. Congo Red removal efficiency and encapsulation capacity of chitosan nanoparticles were determined as above 98% and 5107 mg Congo Red/g chitosan, respectively.

1. Introduction

Dyes are extensively used by textile and dyeing industries such as paper, printing, cosmetic, leather, pharmaceuticals, food and plastic which are the major sources of industrial wastewater [1–3]. Due to dyes being significant pollutants causing environmental and health problems, many investigations have been focused on how to efficiently remove them from wastewater [4–6]. Most of them are toxic, biologically non-degradable and even carcinogenic due to a complex chemical structure and the presence of an aromatic ring in their structure [1,7,8]. Dyes can be classified in three broad categories: (i) anionic (direct, acid and reactive dyes), (ii) cationic (basic dyes) and (iii) nonionic (disperse dyes) [9,10]. Acidic dyes are classified as azo, anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso [11]. Congo Red (sodium salt of benzidinediazo-bis-1-naphtylamine-4-sulfonic acid) is a highly water-soluble, benzidine-based anionic disazo dye and it is reported to be toxic [12,13]. Congo Red which is suspected to be a mutagen and carcinogenic has also been widely used in textile, paper, printing and dyeing rubber and plastic industries and it is the first synthetic dye produced that is capable of dying cotton directly [4,9,14–16].

Although various physical, chemical and biological methods such as adsorption, flocculation/coagulation, biosorption, sonochemical and photochemical degradation, precipitation, membrane filtration, electrochemical techniques, liquid–liquid extraction, oxidation or ozonation, and fungal decolorization have been widely used in the removal of dyes from wastewater, their rapid and effective removal still is an important problem [17–19]. Chitosan, (poly(β-1-4)-2-amino-2-deoxy-D-glucopyranose) is obtained through the deacetylation of chitin which can be extracted from fungal species, insect shells and the exoskeleton of sea creatures such as crayfish, lobster, prawns, crab and shrimp, and it is one of the most abundant biopolymers in nature [6,20–23]. Chitosan is an environmentally friendly, non-toxic, biodegradable, hydrophilic, biocompatible, and antibacterial material and has a flocculating regeneration ability, as well as being economical and in abundance [24–27]. Chitosan has been used in many areas such as wastewater treatment, agriculture, textile, cosmetic, food processing, biochemistry, biotechnology, membrane, microcapsule, nanoparticle, pharmaceutical and biomedical applications [24,28–31].

Chitosan is soluble due to the protonation of the amino groups of glucosamine in an acidic medium and [20] it is crosslinked with various chemical crosslinkers, such as glutaraldehyde (GLA), ethylene glycol diglycidyl ether (EGDE) and epichlorohydrin (ECH) [32]. Chitosan is

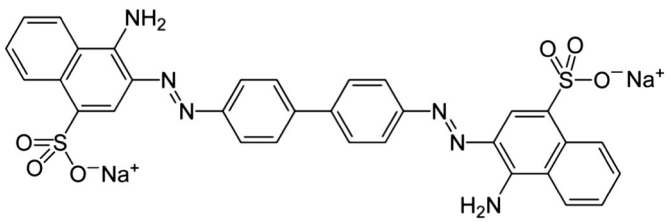

Fig. 1. Chemical structure of Congo Red (CR).

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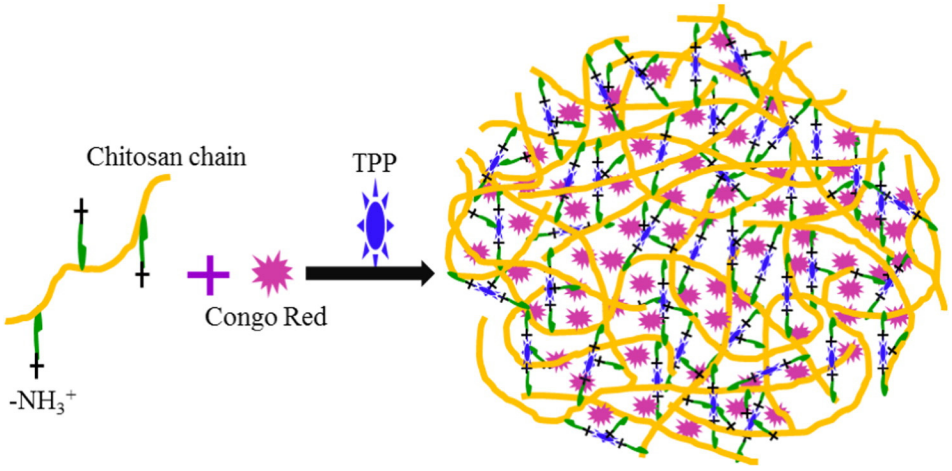

Scheme 1. The schematic representation of the preparation of dye encapsulated chitosan nanoparticles.

also crosslinked ionically with tripolyphosphate (TPP) [33,34]. TPP is a widely used polyanion having a non-toxic and gel forming ability and desirable properties [20,21]. Chitosan nanoparticles can be prepared with ionotropic gelation between chitosan and TPP [28,30,35]. The protonated amine groups of chitosan are crosslinked by inter- and intramolecular bonds with the negatively charged phosphate groups on TPP [20,21].

There are many reported studies on chitosan nanoparticles prepared by ionic crosslinking with TPP that commonly used biological or protein delivery systems [35–37]. From this viewpoint, we used this approach as an alternative method for dye removal from aqueous solutions. For this purpose, chitosan nanoparticles are synthesized in the dye solution during the crosslinking reaction between chitosan and TPP. Thus, it is ensured that the dye molecules are encapsulated within the chitosan nanoparticles which is an affordable and easily accessible material, by using a rapid and efficient method. The effect of the process parameters such as the initial dye concentration, the pH value of the solution, mixing speed/time and TPP concentration on the chitosan nanoparticles is also investigated. Besides this, the storage stability of the dye that is encapsulated by chitosan nanoparticles is determined at different pH values.

2. Experimental

2.1. Chemicals and Reagents

Chitosan (deacetylation degree: ≥75%), sodium-tripolyphosphatepentabasic (TPP), epichlorohydrin and Congo Red (C.I. 22120) (Fig. 1) were obtained from Sigma Aldrich (St. Louis, USA). All other reagents were supplied by Merck (Darmstadt, Germany).

2.2. Dye Removal Experiments

Dye encapsulating experiments were conducted in a series of 250 ml flasks by mixing chitosan with aqueous Congo Red (CR) solutions. In all experiments, the dye solution (50 ml) is prepared at a desired initial concentration by diluting the stock dye solutions with distilled water and transferring them into an Erlenmeyer flask with a magnetic stirrer. The chitosan solution (1 ml, 1% *w*/*v*) was then added to the dye solution and stirred magnetically at 300 rpm. Dye encapsulated chitosan nanoparticles are obtained by adding the TPP solution at different volumes (1% *w*/*v*) to this solution. Dye encapsulated nanoparticles are

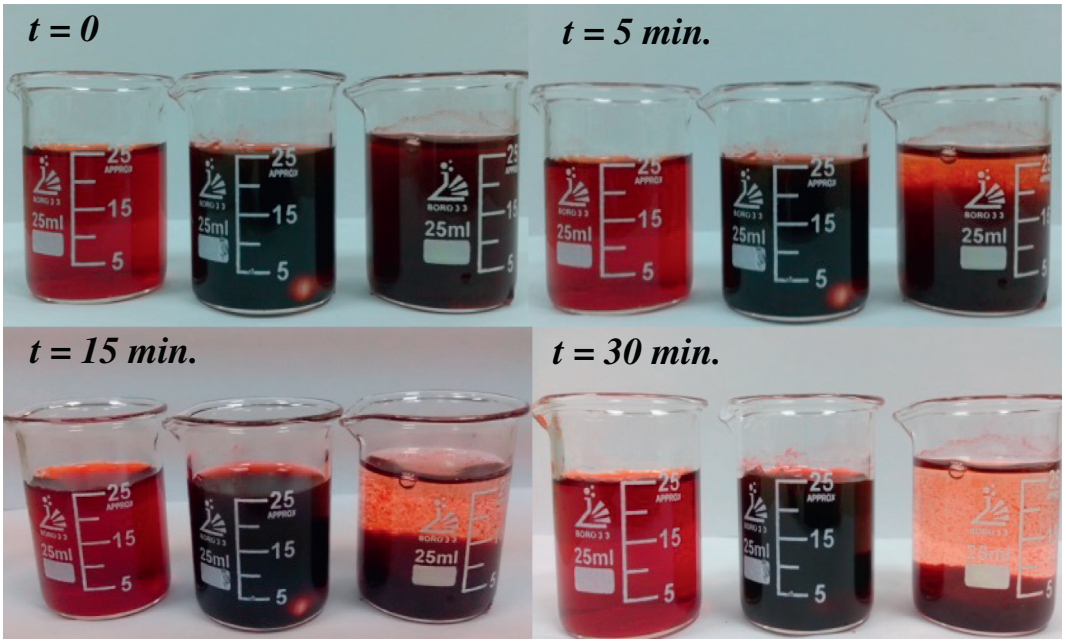

Fig. 2. The photographic images of the precipitation of dye encapsulated CNPs by time.