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The removal of Basic Blue 3 from aqueous solutions by chitosan-based adsorbent: Batch studies

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Abstract

Chitosan-based adsorbent (CHITOD material) is used for the removal of Basic Blue 3 (BB 3) from aqueous solutions. The adsorption of BB 3 on CHITOD material was studied as a function of time, sorbent mass and concentration. The influence of these parameters on the adsorption capacity was evaluated using the batch method. Results of adsorption experiments and kinetic data showed that (i) the CHITOD adsorbent exhibited high sorption capacities toward BB 3; (ii) the Langmuir equation represented the best fit of experimental data; (iii) the dye sorption on material was exothermic and spontaneous in nature; (iv) the kinetic measurements showed that the process was rapid; (v) the adsorption kinetics followed a pseudo-second order model; and (vi) the sorption was dependent on the presence of sulfonate groups. Non-linear method was also found to be more appropriate method for estimating the isotherm and kinetic parameters.

Keywords: Chitosan; Adsorbent; Adsorption; Basic Blue 3; Cationic dye; Batch method; Kinetic and isotherm models; Correlation coefficient; Chi-square

1. Introduction

Chitosan, a linear copolymer composed of (1–4)-linked D-glucosamine and *N*-acetyl-D-glucosamine, is a polysaccharide prepared by *N*-deacetylation of chitin (second abundant polymer in nature after cellulose) [1]. Chitin is obtained from the exoskeleton of crustaceous, the cuticles of insects and the cell walls of fungi. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing.

As a functional biological polymer, chitosan offers an interesting set of characteristics, including non-toxicity, biodegradability, biocompatibility, bioadhesivity, and bioactivity. This material also presents economical advantages (in many countries fishery wastes are low-cost sources and suitable for producing chitosan) and exhibits remarkable physicochemical properties such as an hydrophilic character, a sufficient flexibility of the linear chain, an easy chemical derivatization, a capability to interact and to adsorb various substrates, and cationic properties which are unique among abundant polysaccharides.

Chitosan and its derivatives exhibit innumerable applications in a wide range of fields such as food [2,3], pharmacy [4–6], biomedicine [7–9], cosmetics [10], biotechnology [10,11] and agriculture [10,12]. These versatile materials are also widely applied in the textile, pulp and paper industries [10], and in clarification and water purification [13–24] as coagulating [13,14], flocculating [15,16], chelating [10,17,18] and complexing agents [10,17,18]. Different reviews have recently been reported for wastewater treatment purposes, including metal complexation [19,20], dye removal [21], complexing adsorbent matrices [22,23], and membranes [24].

As already mentioned, chitosan has widely been studied for pollutant adsorption from aqueous solutions: the cationic character, along with the presence of reactive functional groups in polymer chains, has given it particular possibilities as efficient adsorbent agents. It is evident from the abundant literature data

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Nomenclature

a_L	Langmuir isotherm constant (l/mg)
A	Temkin isotherm constant (l/g)
B	Temkin isotherm constant
C_e	liquid phase dye concentration at equilibrium (mg/l)
C_o	initial dye concentration in liquid phase (mg/l)
k_1	equilibrium rate constant of pseudo-first order sorption (min^{-1})
k_2	equilibrium rate constant of pseudo-second order sorption (g/mg min)
k_i	intraparticle diffusion rate constant (mg/g min$^{-1/2}$)
K	saturation constant (mg/l)
K_F	Freundlich constant (l/g)
K_L	Langmuir isotherm constant (l/g)
m	mass of adsorbent used (g)
n	cooperative binding constant
n_F	Freundlich isotherm exponent
q_e	amount of dye adsorbed at equilibrium (mg/g)
q_{max}	maximum adsorption capacity of the adsorbent (mg/g)
q_t	amount of dye adsorbed at time t (mg/g)
r^2	non-linear correlation coefficient
R^2	linear correlation coefficient
t	time (min)
t_e	equilibrium time (min)
V	volume of dye solution (l)
x	amount of dye adsorbed (mg)

Greek symbols

α	initial adsorption rate (mg/g min)
β	Elovich desorption constant (g/mg)
χ^2	Chi-square test statistic

that this biomaterial offers a great potential in the adsorption field and might be a promising adsorbent for environmental purpose [19–22]. In particular, one of the major applications is based on its ability to bind strongly heavy and toxic metals. It represents an attractive alternative to other conventional commercial adsorbents because of its low cost and local availability, high reactivity, excellent chelation behavior and high selectivity towards heavy metals [17,19,20].

Chitosan is also known as an effective adsorbent for proteins [25], saccharides [26], drugs [27], oils [28], bacterial suspensions [29], phenolic derivatives [17,30,31], and also for dye wastewater removal [10,21]. In recent years, numerous studies on chitosan-based biomaterials for dye removal demonstrated that these versatile biosorbents are efficient and have a high affinity for many classes of dyes [32–47], including acid, direct, mordant, reactive and disperse dyes (Table 1). However, only a limited number of published studies can be found on the use of chitosan as an adsorbent for cationic (basic) dye removal.

In this paper, we propose chemical grafting of sulfonate groups onto chitosan as a means to confer the ability to adsorb basic dyes, in particular Basic Blue 3 (BB 3). Several adsorption and kinetic studies are presented and discussed here. The equilibrium data were analyzed using Freundlich, Langmuir, Temkin and Generalized isotherms. In order to investigate the mechanism of sorption, adsorption data were modeled using the pseudo-second order kinetic equation, Elovich equation and intraparticle diffusion model. The characteristics parameters for each model were determined. A comparison was made between the linear and non-linear methods of estimating isotherm and kinetic parameters.

2. Experimental

2.1. Adsorbents

Two chitosan-based sorbents, namely CHITO and CHITOD, were used in this study. Their characteristics are reported in Table 2. CHITO (prepared from crab shells, degree of acetylation = 20%) was supplied by Protan (USA). CHITOD was prepared in one step by reacting chitosan with 4-formyl-1,3-benzene sodium disulfonate in the presence of sodium cyanoborohydride (Fig. 1). The synthesis of CHITOD has already been described in detail in previous works [48,49].

2.2. Dye

The sorption capacity was investigated using C.I. Basic Blue 3 (BB 3, Classification Number 51004; chemical class monox-

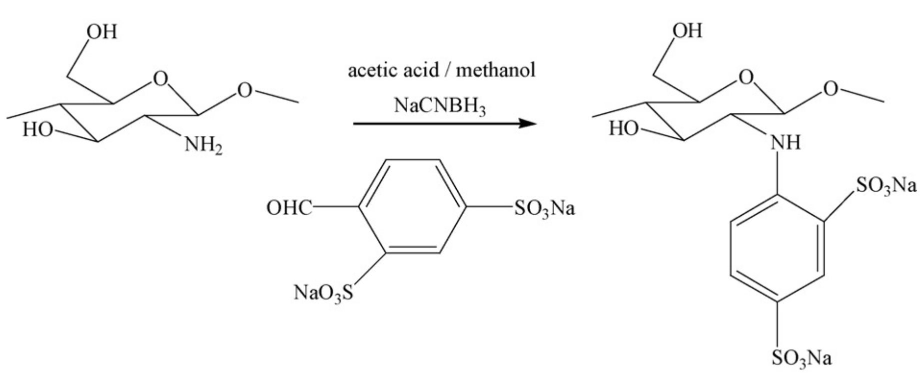

Fig. 1. Synthesis of CHITOD.