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Adsorption of food dyes from aqueous solution by glutaraldehyde cross-linked magnetic chitosan nanoparticles

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ABSTRACT

Glutaraldehyde cross-linked magnetic chitosan nanoparticles (GMCNs) were prepared through cross-linking modification of magnetic chitosan nanoparticles (MCNs) using glutaraldehyde as crosslinker, that not only exhibited excellent food dyes adsorption performance, but also showed low cytotoxicity. Adsorption characteristics of GMCNs in FD&C Blue 1 and D&C Yellow 5 aqueous solutions have been studied and results indicated that the adsorption capacities were affected by initial pH values, initial dye concentrations and temperatures. Food dyes adsorption followed with the pseudo-second-order reaction, and equilibrium experiments were well fitted the Langmuir isotherm model. Maximum adsorption capacities of GMCNs displayed at pH 3.0 and at 25 °C, being up to 475.61 and 292.07 mg/g, for FD&C Blue 1 and D&C Yellow 5 respectively. Thermodynamic results demonstrated that the adsorption processes were spontaneous and exothermic. Furthermore, it was found that the GMCNs can be regenerated and reused through dye desorption in alkaline solution.

1. Introduction

Food dyes as a member of food additives, are widely used as colorant in food, cosmetic and drug industries, to produce dyeing sweets, chewing gums, puddings, juices, mustard, sodas, drugs and cosmetics (Piccin et al., 2009). However, approximately 10–20% of the dyes are lost during manufacturing process, result in large amounts of wastewater (Gao et al., 2011a). In addition, food dyes residues in waste effluents are adversely affect aquatic environment by coloring water and impeding light penetration, and are suspected to cause carcinogenic effects, hypersensitivity reactions and genotoxic effects on human health (Gao et al., 2011b; Kobylewski and Jacobson, 2012). Furthermore, that dyes in wastewater are difficult to be treated, because these dyes are recalcitrant molecules and resistant to aerobic digestion. Hence, numerous conventional treatment including coagulation, precipitation, membrane filtration, oxidation, adsorption, and photodegradation have been utilized to remove or eliminate dyes from wastewater (Crini and Badot, 2008; Robinson et al., 2001). Particularly, adsorption process is considered to be an effective and economical procedure to remove food dyes from industrial effluents.

A large variety of adsorbent materials have been studied to reduce dye concentration in aqueous solution, such as activated carbon (Ozsoy and van Leeuwen, 2010; Piccin et al., 2012), chitosan (Debrassi et al., 2012; Piccin et al., 2011), cellulose (Tabara et al., 2011), inorganic oxides (Siwinska-Stefanska et al., 2012) and anaerobic sludge (Yu et al., 2011). Chitosan, as an effective dye adsorbent, has received much scientific attention recently and been widely used for food dyes removal from wastewater due to its relatively low cost, high adsorption capacity and rate, the superiorities are ascribe to the presence of large amounts of amino groups ($-NH_2$) on chitosan molecules (Chen and Chen, 2009; Dotto and Pinto, 2011b; Kyzas and Lazaridis, 2009). However, chitosan is diffluent in dilute organic acids such as formic acid, acetic acid and the like, because its amino groups are fully protonated at approximately pH 3.0, and the polymer chains with positive charges fall apart in the solution. In this case, cross-linking modification of raw chitosan with epichlorohydrin or glutaraldehyde is a good way to improve the chemical stability of chitosan in acid solution, and the adsorption selectivity and capacity of food dyes from industrial effluents (Chen and Chen, 2009; Rosa et al., 2008).

Although crosslinked chitosan has an enhanced stability and adsorption capacity of food dyes, their low separation efficiency in aqueous solution is still affect their industrial application scopes. Meanwhile, magnetic separation technology has attracted much attention for its easy separation procedure and high separation efficiency from aqueous solution by applying an external magnetic field (Rocher et al., 2010). In addition, nano-scaled magnetic chitosan particles, as the adsorbents for food dyes adsorption, have overcome the limitation of micro-scaled particles. The nano-scaled

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Nomenclature

b_F	adsorption intensity defined in Eq. (5)
C_e	equilibrium concentration of dye (μg/mL)
C_f	final concentration of dye (mg/mL)
C_i	initial concentration of dye (mg/mL)
E	mean adsorption energy defined in Eq. (8) (kJ/mol)
k_1	pseudo-first-order rate constant defined in Eq. (2) (min^{-1})
k_2	pseudo-second-order rate constant defined in Eq. (3) (mg/g min)
K	Dubinin–Radushkevich constant defined in Eq. (6) (J^2/mol^2)
K_F	Freundlich constant (mg/g)
K_L	Langmuir constant defined in Eq. (4) (L/mg)
Q	adsorption capacity (mg/g)
Q_{DR}	Dubinin–Radushkevich maximum adsorption capacity of dye (mg/g)
Q_e	adsorption capacities of dye at equilibrium (mg/g)
$Q_{e,cal}$	calculated equilibrium adsorption capacities (mg/g)
Q_t	adsorption capacities of dye at a given time t (mg/g)
Q_m	Langmuir maximum adsorption capacity of dye (mg/g)
R	universal gas constant (8.314 J/K mol)
R^2	liner correlation coefficient
T	temperature in Kelvin (K)
V	volume of dye solution (mL)
W	weight of the crosslinked magnetic chitosan nanoparticles used (g)
ε	Polanyl potential defined in Eq. (7)
ΔG^o	Gibbs free energy of the adsorption defined in Eq. (10) (kJ/mol)
ΔH^o	standard enthalpy changes defined in Eq. (9) (kJ/mol)
ΔS^o	standard entropy changes defined in Eq. (9) (J/mol K)

particles contrarily provide large surface area to increase dyes adsorption capacity and decrease the internal diffusion resistance (Zhou et al., 2011). From the above, magnetic chitosan nanoparticles (MCNs) are chosen for food dyes adsorption.

Crosslinkers such as epichlorohydrin (ECH) and glutaraldehyde (GA) can be used to modify MCNs to ensure their high adsorption capacity and good stability, Zhou et al. (2011) employed ethylenediamine to modify MCNs for acid dye adsorption purpose by using ECH as the crosslinker during preparation. However, the potential influence of crosslinker modified MCNs used for food dyes adsorption on environment and human health need to be considered. Therefore, GA was chosen as a modification crosslinker to prepare glutaraldehyde cross-linked magnetic chitosan nanoparticles (GMCNs) for its no carcinogenicity compared with epichlorohydrin. In addition, GA helps chitosan to form quaternary structure on the surface of MCNs, so as to increase the content of protonated amino groups ($-NH_3^+$) to adsorb the anionic food dyes (Rosa et al., 2008).

In the present study, the GMCNs were prepared through crosslinking modification of MCNs using GA as the crosslinker to facilitate the formation of chitosan quaternary structure on GMCNs, the effect of GA concentration on food dyes adsorption capacities and cytotoxicities of the GMCNs was comprehensive evaluated. In addition, the adsorption characteristics of FD&C Blue 1 and D&C Yellow 5 from aqueous solutions on GMCNs were investigated. Furthermore, the influence factors such as pH, dye concentrations and temperature to adsorption were studied; the equilibrium isotherms, thermodynamic parameters and regeneration were determined and discussed.

2. Methods

2.1. Chemicals and regents

Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$), ammonia water (NH_4OH), sodium hydroxide, acetic acid (99.7+%), cyclohexane, and sodium chloride were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Chitosan (low molecular weight) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Triton X-100, *n*-hexanol, glutaraldehyde (25%) were purchased from Alfa Aesar (Heysham, Lance, UK). RPMI-1640 media and dimethylsulfoxide (DMSO) were purchased from Thermo Scientific. FD&C Blue 1 and FD&C Yellow 5 were obtained from Emerald Performance Materials (Cincinnati, OH, USA) and their structures are presented in Fig. 1. All regents were analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of the adsorbent

The GMCNs were prepared starting from MCNs, and MCNs were prepared by two-step route using Triton X-100 reversed-phase water-in-oil microemulsion system (Zhou et al., 2013). Fe_3O_4 nanoparticles were prepared by coprecipitating. Cyclohexane, *n*-hexanol, 10 mg/mL chitosan 2% acetic acid solution and Fe_3O_4 turbid liquid were mixed (11:6:4:4) in a beaker at 1800 rpm, and then Triton X-100 was added to form a bright black-colored microemulsion. After with quickly addition of 20 mL 5 mol/L NaOH solution, mixture were placed at a 60 °C water bath for 2 h, then MCNs were collected with a magnet and rinsed with ethanol and then deionized water for three times. Finally, 1 mg/mL MCNs were modified by adding different concentrations of GA (0, 0.025, 0.075, 0.125, 0.25, 0.375, 0.5, 0.75 and 1 mol/mL) with a shaking of 150 rpm for 60 min at room temperature to obtain different GMCNs. The GMCNs were intensively washed by deionized water to remove unreacted GA, and then freeze-dried for further experiment.

2.3. Adsorption of food dye

The different GMCNs were prepared by adding different concentrations of GA to study their adsorption capacities of two food dyes which are FD&C Blue 1 and FD&C Yellow 5. The adsorption processes were carried out by adding 50 mg GMCNs into 50 mL of 200 μg/mL dye solution at pH 6.6 with a shaking of 150 rpm for 60 min at room temperature. The adsorbents were removed by a 1 T magnet nearby (Sigma–Aldrich, St. Louis, MO, USA). The supernatant of dye solutions was adjusted to a pH level of 6.0 using HCl or NaOH solutions, the dye concentration was determined using spectrophotometry at wavelength of 408 nm for FD&C Blue 1 and 428 for FD&C Yellow 5 by a micro plate reader (Molecular Devices, Sunnyvale, CA). The adsorption capacity (Q) was calculated through following equation:

$$Q = \frac{(C_i - C_f)V}{W} \tag{1}$$

2.4. Cytotoxicity

Human hepatocellular carcinoma cell line HepG2 was obtained from American Type Culture Collection (HB-8065, Manassas, VA)