Chemical Engineering Journal 287 (2016) 410–418

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Fast removal of methylene blue from aqueous solution using porous soy protein isolate based composite beads

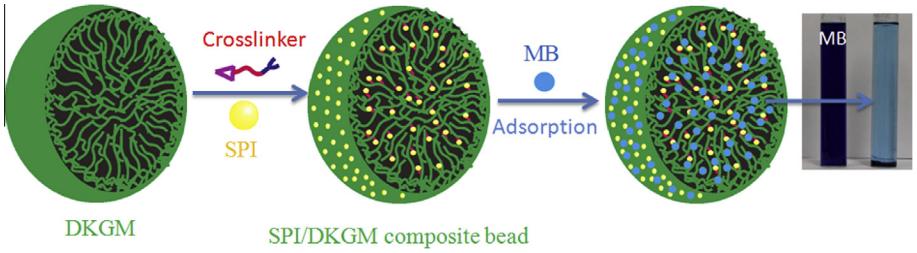
Feng Liu [a,*], Hailiang Zou [a], Jinwen Hu [b], Hongbo Liu [a], Jianbing Peng [a], Yanwu Chen [a], Fenghui Lu [a], Yingpeng Huo [a]

[a] College of Applied Chemical Engineering, Shunde Polytechnic, Foshan 528333, PR China
[b] Key Laboratory of Cellulose Lignocellulosics Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

HIGHLIGHTS

- We reported a novel porous composite adsorbent.
- High adsorption capacity and fast adsorption of MB by the adsorbent are achieved.
- Maximum sorption capacity for MB by the adsorbent was 272.4 mg g^{-1}.
- The adsorption of MB onto the adsorbent was exothermic and spontaneous.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form 8 November 2015
Accepted 13 November 2015
Available online 19 November 2015

Keywords:
Soy protein isolate
Konjac glucomannan
Methylene blue removal

ABSTRACT

Soy protein isolate (abbreviated as SPI) was chemically immobilized on deacetylated konjac glucomannan (abbreviated as DKGM) in the current work. The obtained porous SPI/DKGM composite beads were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR) and zeta potential analysis. Adsorption performances of porous SPI/DKGM composite beads were tested to remove methylene blue from aqueous solution. Benefiting from the combined merits of SPI, high adsorption capacity and fast adsorption of methylene blue (MB) by porous SPI/DKGM composite beads are achieved. The maximum methylene blue adsorption capacities were shown to be 272.4 mg g^{-1} for porous SPI–DKGM composite beads. These results confirm that the porous SPI–DKGM composite beads have a potential for methylene blue removal from wastewater.

1. Introduction

Freshwater contamination with dyestuff is becoming a great environmental problem. Dyes are widely used in various industries, such as textile, paper, leather tanning, paint, printing and cosmetics [1]. The increasing industrial growth is the major source of dyestuff introduction into freshwater. Most dyes are complex organic molecules and chemically synthesized. They can be classified into three major types as anionic, cationic and non-ionic disperse dyes. Methylene blue (MB) as a type of cationic dyes is widely used in many fields such as dyeing, monitoring and printing. MB discharges into freshwater give undesirable color to hydrosphere which may reduce sunlight penetration and affect photosynthetic activity in aquatic life. MB hazardous effects can cause health problems, such as skin irritation, increased heart rate on inhalation and cancer [2].

Commonly accepted technologies for the removal of MB from wastewater include adsorption [3], photocatalytic oxidation [4], photocatalytic degradation [5,6] and membrane separation treatment [7,8]. Each technology has its own advantages and disadvantages. Adsorption has been found to be superior to other techniques in terms of low cost, simplicity of design and ease of operation. There has been increased focus on developing new

* Corresponding author.
E-mail address: liufenglf_2003@qq.com (F. Liu).

http://dx.doi.org/10.1016/j.cej.2015.11.041
1385-8947/

adsorbents with high adsorption capabilities for MB removal from wastewater stream, such as graphene oxide [9–11], nanotubes [12], nanocomposite [13,14], activated carbon [15–17], metal oxide [18–20], bioadsorbents [21–23]. Moreover, composite adsorbents are emerging as a new generation of adsorbent for dye removal because the inherited disadvantages of the individual adsorbents might be minimized by combining them [24–27].

Soy protein isolate (SPI) extracted from Soybean is currently one of the most abundant sources of plant proteins. The major components of SPI are of Glycinin (7S) and β-conglycinin (11S), in which there consist of 20 different amino acids, such as aspartic, lysine, phenylalanine, leucine, glutamic acid and tyrosine [28]. SPI has been reported to exhibit desirable functionalities, and its wide application as biodegradable package has been well documented [29]. Nanoparticles synthesized from SPI have been expected to be suitable drug delivery systems because of nutrition and safety [30–32]. Soy protein isolate (SPI) with good metal-chelating properties has a significant potential as a biosorbent for removal of heavy metals from wastewater [33]. Although SPI shows great potential as adsorbent, it suffers from drawbacks such as high solubility in acidic solutions or basic solution and inadequate mechanical properties [29,34].

Konjac glucomannan (KGM), a natural polysaccharide derived from the tubers of Amorphophallus konjac, consists of D-mannose and D-glucose in a molar ratio of 1.6:1 with a β-1,4-linkage and contains acetyl group per every 12 or 18 repeating units [35,36]. The most important feature of KGM lies on acetyl groups on KGM. Hydrogels of KGM with cross-linked network are formed after deacetylation in alkaline condition [37]. Hydrogels of KGM containing various functionalities and porosities are stable in most organic solvents, allowing them also to be suitable for environmental applications [38].

Hydrogels of deacetylated konjac glucomannan (DKGM) with three-dimensional crosslinked networks are able to absorb and retain water soluble SPI biomacromolecules. SPI biomacromolecules can further be immobilized onto DKGM using crosslinking agents. As hydrogels of DKGM possess amine functional groups, they can absorb cationic dyes such as MB. In the present work, we aim to design porous SPI/DKGM composite beads as an efficient composite adsorbent for dye removal. Hydrogel of DKGM with supramolecular architectures endows it with porosities to use as an immobilization matrix for SPI impregnation. The adsorption of MB onto porous SPI/DKGM composite beads, including effects of pH, dosage, contact time, temperature and initial MB concentration, was systematically investigated by batch adsorption experiments. We also thoroughly studied the kinetics, isotherms and thermodynamics of adsorption process.

2. Experimental

2.1. Materials

Refined KGM powders were purchased from Mianyang Anxian Dule Company and were used without further purification. SPI powders containing 88% protein (dry basis) were purchased from Shanghai Jiaoyuan Industrial Co., Ltd and were used without further purification. All other chemicals (epichlorohydrin, isopropanol, alcohol, sodium hydroxide, hydrochloric acid, methylene blue, etc.) used in this work were all of analytical grade and obtained from Aladdin Reagent of China.

2.2. Preparation of DKGM

DKGM was synthesized following a modified literature method [39]. KGM flour (20.0 g) and sodium hydroxide (0.35 g) were dispersed in 120 mL alcohol/water mixture solution (50:70 V/V) in a three-necked round-bottomed flask (250 mL) equipped with a mechanical stirrer. The reaction mixture was stirred (400 rpm) at 50 °C for 12 h. The obtained product was filtered out and washed with distilled water, and then dried under vacuum for 48 h, yielding 18.8 g of the product as white powders in a 94% yield.

2.3. Preparation of SPI/DKGM composite beads

SPI (8.0 g), sodium hydroxide (8.0 g) and distilled water (40.0 mL) were mixed and stirred mechanically at 60 °C for 30 min in a three-necked round-bottomed flask (500 mL). This was followed by the addition of 8.0 g of DKGM. The mixture was stirred at 60 °C for 2 h. Under mechanical stirring at 400 rpm, 400.0 mL of isopropanol was added into the flask. Subsequently, 12.0 mL of epichlorohydrin was introduced into the flask using a syringe. The cross-linking reaction was allowed to proceed for 15 h. After 15 h, SPI/DKGM composite beads was filtered out of reacted system and washed thoroughly with distilled water in order to remove free SPI that may be attached to the surface of DKGM powder. The product was dried to a constant weight (10.8 g) at 100 °C.

2.4. Characterization

The micrographs of SPI, DKGM and SPI/DKGM composite beads were observed by a HITACHI-SU8010 scanning electron microscopy (SEM).

A Nicolet -6700 model FT-IR spectrometer was used to record FTIR spectra for functional group analysis of the natural DKGM, SPI, SPI/DKGM composite beads, MB absorbed SPI/DKGM composite beads and MB samples.

Zeta potentials of SPI/DKGM composite beads were determined by a Nano-ZS Zetasizer (Malvern, UK) following the literature method [38]. Dry SPI/DKGM composite beads (0.25 g) were added in KNO_3 solution (50 cm^3, 10^{-3} M). The pH of the mixture was adjusted between 2.0 and 8.0, using potassium hydroxide (0.10 M) or hydrochloric acid (0.10 M). The mixture was magnetically stirred for 30 min. The supernatant was collected via transfer pipetting for zeta potential measurements.

A Shimadzu UV-2550 spectrophotometer was used to determine the concentrations of MB left in supernatant solutions referring to the standard curve of MB at the maximum wavelength (665 nm) of MB dye.

Water absorbencies of DKGM and SPI/DKGM composite beads were determined following the literature method [38].

The protein content of dried SPI/DKGM composite beads samples was measured by the micro-Kjeldahl method and nitrogen to protein conversion factor of 6.25 was used for calculation following the literature method [40].

2.5. Bath experiments

The samples of SPI/DKGM composite beads were used for adsorption study regarding the effects of initial pH, adsorbent dosage, contact time, temperature and initial MB concentration. All of the following adsorption experiments were done in triplicate in a 250 mL stoppered conical flask containing 50.0 mL of MB solution. Initial MB solutions with different concentrations were prepared by proper dilution from stock MB standards (1000 mg L^{-1}). The pH of initial MB solution was adjusted by sodium hydroxide (0.10 M) and hydrochloric acid (0.10 M). A certain amount of the adsorbent was added and the mixture in the flask was shaken for a predetermined contact time on a platform constant shaking incubator at 200 rpm. Samples were taken and filtered, and the MB concentrations of the filtrates were measured by a Shimadzu