Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Adsorptive removal of multi-azo dye from aqueous phase using a semi-IPN superabsorbent chitosan-starch hydrogel

Fahanwi Asabuwa Ngwabebhoh, Mustafa Gazi, Akeem Adeyemi Oladipo*

Department of Chemistry, Eastern Mediterranean University, Gazimagusa, TRNC via Mersin 10, Turkey

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 12 June 2016
Accepted 26 June 2016
Available online 1 July 2016

Keywords:
Semi-interpenetrating
Superabsorbent
Hydrogel
Chitosan-Starch
Direct Red 80

ABSTRACT

This article reports the efficient removal of Direct Red 80 (DR80) dye from aqueous phase using a semi-interpenetrating network (IPN) superabsorbent chitosan-starch (ChS) hydrogel. In the present investigation, the influence of initial pH, ChS dose, initial dye concentration, temperature and effect of salts on the sorption of DR80 dye was evaluated. A maximum swelling capacity of 15 g/g was determined for ChS hydrogel. The sorption equilibrium data demonstrated good agreement with Freundlich isotherm. The sorption process best fitted the pseudo-second order kinetic model. Maximum uptake capacity of the hydrogel was determined as 312.77 mg/g. The mean sorption energy (E = 11.34–14.9 kJ/mol) demonstrated that DR80 sorption was mainly chemisorption. The temperature dependence data revealed the sorption process was spontaneous, endothermic and favourable at higher temperature based on the enthalpy (ΔH° = +83.68 kJ/mol) value obtained. Boyd model confirmed intra-particle diffusion was the limiting step for DR80 uptake. In addition, sorption/desorption studies were performed to investigate the reusability of ChS hydrogel which demonstrated significant sorption for four consecutive cycles.

1. Introduction

In recent years, biopolymers such as starch, pullulan, alginate, cellulose, chitin, chitosan have been extensively applied in areas of biomedicine, packaging, drug delivery systems, tissue engineering and wastewater purification (Pourjavadi et al., 2009). This class of polymers has also served as a major backbone of naturally derived superabsorbent hydrogel (SAH) (Sadeghi and Soleimani, 2011; Zohuriaan-Mehr and Kabiri, 2008). SAHs of recent have gained great attention due to typical properties such as high water retention capacity, fast sorption rate and good gel strength. These properties exhibited by SAHs have led its applications in several areas such as wound healing, agriculture, water purification and drug delivery (Dhanapal and Subramanian, 2015; Ferfera-Harrar et al., 2014). However, SAHs are moderately crosslinked 3D hydrophilic network polymeric materials with properties to absorb and retain large amount of water or other aqueous fluids in aqueous environment with swelling of up to a hundred and more times its original size even under certain conditions such as heat or pressure with the ability to maintain its physical structure without dissolving (Ngwabebhoh, 2014; Saber-Samandari et al., 2012; Yildiz et al., 2010).

Chitosan is an amino polysaccharide derived from total or partial deacetylation of chitin extracted from the exoskeletons of marine crustaceans to generate a linear structure of repeating glucosamine (2-amino-2-deoxy-β-D-glucopyranose) and N-acetyl-glucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) joined in a beta (1,4) array (Bhatnagar and Sillanpää, 2009; Prashanth and Tharanathan,

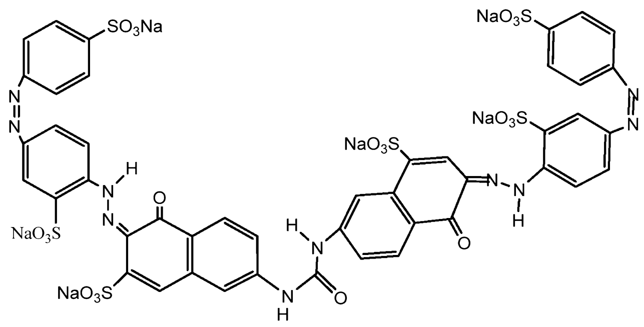
* *Corresponding author*. Tel.: +90 5317766027.
E-mail address: asabuwa.nf@gmail.com (F.A. Ngwabebhoh).
http://dx.doi.org/10.1016/j.cherd.2016.06.023

Nomenclature

C	intra-particle diffusion constant (mg/g)
K_1	pseudo first-order kinetic rate constant (min^{-1})
K_2	pseudo second-order kinetic rate constant (g/mg min)
K_{IP}	intra-particle rate constant (mg/g min)
α	Elovich adsorption coefficient (mg/g min)
β	Elovich adsorption constant (g/mg)
K_L	Langmuir sorption constant (L/mg)
K_F	Freundlich constant (mg/g)(L/mg)
A_T	Temkin isotherm equilibrium binding constant (L/mg)
b_T	Temkin isotherm constant
B	heat of sorption constant (J/mol)
K_{DR}	Dubinin–Radushkevich constant (mol^2/kJ^2)
M	mass of adsorbent (mg)
n	sorption intensity
V	volume of adsorbate (L)
C_o	initial concentration of adsorbate (mg/L)
C_e	equilibrium concentrations of adsorbate (mg/L)
C_s	concentration of dye on adsorbent (mg/L)
q_e	equilibrium adsorbed capacity of adsorbent (mg/g)
$q_{e,exp}$	experimental equilibrium adsorbed capacity (mg/g)
Q_o	maximum sorption capacity (mg/g)
R	ideal gas constant (8.314 J/mol K)
r^2	coefficient of determination
T	absolute temperature (K)
t	time (min)
E	mean free energy (kJ/mol)
ΔG°	Gibbs energy change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
ΔS°	entropy change (J/mol K)

2007). The derived chitosan is non-toxic, biodegradable, biocompatible and has been investigated by several researchers for suitable applications (Bhattarai et al., 2010; Chatterjee and Woo, 2009; He et al., 2016; Liu and Lin, 2010; Vakili et al., 2016). This biopolymer has proven to be an efficient adsorbent in wastewater treatment for sorption of heavy metal ions and dyes from aqueous solution supported by two distinct advantages: low cost and its outstanding chelating ability (Crini and Badot, 2008; Zhu et al., 2012).

Starch another abundant and interesting biopolymer is a polysaccharide consisting of D-glucose units generally referred as homoglucan or glucopyranose has been in used from 1970s (Abdel-Halim and Al-Deyab, 2014; Lu et al., 2009). This biopolymer is chemically composed of amylose (10–30%) a linear polysaccharide with D-glucose units joined by alpha (1,4) linkages of varying molecular weight ranging from 10^5 to 10^6 g/mol and amylopectin (70–90%) a highly branched polysaccharide consisting of alpha (1, 6) linkages occurring every 24–79 glucose units (Avérous and Pollet, 2012; Li et al., 2013; Subramanian et al., 2014). However, due to properties such as biodegradability, cost effectiveness, biocompatibility and non-toxicity, several studies have been previously performed on starch for application in areas of film packaging, tissue engineering, drug delivery, food additives, agriculture, heavy metal and dye sorption (Soto et al., 2015; Torres et al., 2011).



Scheme 1 – Molecular structure of DR80 dye.

Direct Red 80 (DR80) is a food anionic dye composed of 7,7-(Carbonyldiimino) bis [4-hydroxy-3-((2-sulfo-4-[azo (4-sulfophenyl) phenyl) azo-2-naphthalene sulfonic acid] hexasodium salt (Scheme 1) and belongs to the class of azo dyes with maximum sorption wavelength of 530 nm. This dye is a complex unsaturated aromatic compounds of varying chemical composition and characterized by high color intensity, substantiveness and fastness in coloring (Hunger, 2007; Suyamboo and Perumal, 2012). This azo dye with one or several benzene rings leads to low degradation and eventually formation of toxic byproducts. Thus, discharge of these dyes into the environment maybe considered toxic and can act as vital pollutants to aquatic ecosystems. Several treatment techniques such as solvent extraction, sorption, chemical coagulation and photocatalytic degradation have been developed for the removal of these contaminants. Amongst all the techniques, sorption is most widely used due to its simplicity and time effectiveness.

Several studies on the sorption of anionic dyes from aqueous solutions have been previously investigated using chitosan hydrogel as the adsorbent (Liu et al., 2015; Nesic et al., 2012). But due to limitations such as low mechanical properties and specific gravity exhibited by chitosan leads to slow sorption rate and swelling capacity of this hydrogel in water (Ngwabebhoh et al., 2016; Sakaew and Umpuch, 2013). The main objective of this present study was to synthesize chemically crosslinked chitosan hydrogel via formation of a semi-IPN with starch which enhanced the hydrogel stability and swelling capacity. Though some research studies have been reported on chitosan-starch related materials (Li et al., 2013; Ramasubramaniam et al., 2014), this study is aimed at fabricating a semi-IPN superabsorbent ChS hydrogel characterized with improved swelling and sorption capacity in aqueous solution. The performance of the hydrogel is then evaluated for the removal of DR80 dye from aqueous phase. Kinetics, isothermic models and thermodynamics were investigated to best describe the sorption process. In addition, sorption/desorption studies were performed to evaluate the reusability of the hydrogel.

2. Materials and methods

2.1. *Materials*

Starch powder of molecular weight 342.30 g/mol and repeating molecular unit of $(C_6H_{10}O_5)_n$ was purchased from Merck. Chitosan of molecular weight 4.8×10^5 g/mol with deacetylation 85% with 200–800 cPs, glutaraldehyde (25%, v/v), glacial acetic acid (100%, v/v), NaOH, HCL (37%, v/v), Direct Red 80 dye (M_{wt}