Schiff Base - Chitosan Grafted L-Monoguluronic Acid as A Novel Solid-phase

Adsorbent for Removal of Congo Red

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Abstract

A novel modified chitosan adsorbent (GL-SBCS) was synthesized by covalently grafting a Schiff base-chitosan (SBCS) onto the surface of L-Monoguluronic acid. Physic-chemical investigation on the adsorption of congo red, an anionic azo dye by GL-SBCS has been carried out. The effect of different weight contents of chitosan in GL-SBCS composite, adsorbent dosage, initial pH and contact time were studied in detail using batch adsorption. Results showed that GL-SBCS exhibited better than normal CS and L-Monoguluronic acid. Further investigation demonstrated that the adsorption pattern fitted well with the Langmuir model ($R^2 > 0.99$) but less-satisfied the Freundlich model. Both ionic interaction as well as physical forces is responsible for binding of congo red with GL-SBCS as determined by zeta potential measurement Both sodium chloride and sodium dodecyl sulfate significantly influenced the adsorption process. SBCS would be a good method and resource to increase absorption efficiency for the removal of anionic dyes in a wastewater treatment process.

Keywords

L-Monoguluronic acid ; Schiff base chitosan; Congo red;

1. Introduction

Synthetic dyestuffs widely exist in the effluents of industries such as textiles, printing, paper, plastics and leather. Many dyes and pigments contain aromatic rings in their structures, which make them toxic, non-biodegradable, carcinogenic and mutagenic for aquatic systems and human health ^[1, 2]. Congo red [1- naphthalene sulfonic acid, 3, 3'-((4,4'-biphenylenebis (azo)) bis (4-amino-)) disodium salt is a common benzidine-based dye in Chinese printing and dyeing industry. This dye has been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen. Synthetic dyes such as congo red (CR) are difficult to biodegrade due to their complex aromatic structures, which convey physico-chemical, thermal and optical stability^[2,3]. Some conventional physical-chemical methods such as reverse osmosis, ion exchange, chemical precipitation or lime coagulation, and oxidation are all used widely in wastewater treatment. However, the application of these techniques has been restricted due to high-energy consumptions or expensive synthetic resins and chemicals. There are many processes to remove congo red molecules from colored effluents and these treatment methods can be divided into three categories: (1) physical methods such as adsorption^[4]; (2) chemical methods such as ozonation^[5], photo degradation^[6] and electrochemical process^[7]; and (3) biodegradation^[8]. Moreover, these methods generate large a amount of toxic sludge and are ineffective at lower concentrations of dye ^[9,10]. Therefore, there is an urgent requirement for development of innovative, but low cost processes, by which dye molecules can be removed.

Adsorption techniques are a quite popular due to their simplicity and highly effective methods for removal of dye from wastewater ^[11] (Allen et al., 2004) and the adsorbent was frequently used in the treating processes. The adsorption adsorbent for removal of dyestuffs from wastewater include activated carbon, montmorillonite, bentonite, rice hull ash, leaf, fly ash, activated red mud, rice husk and fungi^[12-18]. Those methods have been used for the removal of congo red from aqueous solutions. However, some of these adsorbents do not have good adsorption capacities for anionic dyes because most have hydrophobic or anionic surfaces. Hence, there is a need to search for more effective adsorbents.

Chitosan, a linear biopolymer of glucosamine, has exhibited excellent adsorption capacity for anionic dyes and heavy metal ions because chitosan molecules contain a large number of active amine ($-NH_2$) groups. Further, chitosan has one of the highest adsorption capacities towards many classes of dyes ^[19], is the second most abundant biopolymer in nature and obtained on an industrial scale by chemical deacetylation of crustacean chitin. Chemical modification of chitosan can improve the adsorption capacity of chitosan beads. In this context, cross-linking and insertion of new functional groups ^[20,21] have been performed. However, surfactant impregnation of chitosan modification for the adsorption of congo red has not been previously reported.

In this study, we describe the synthesis and characterization of the composite L-Monoguluronic acid-Schiff base-chitosan (GL-SBCS) prepared by covalent modification of L-Monoguluronic acid with the Schiff base chitosan. We also

developed a method for the adsorption of congo red dye and compared its adsorption capacity with other two common absorbers.

2. Methods

2.1. Materials

Chitosan (CS, >85% de-acetylation) and Congo red used in this study were purchased from Kelong Chemical Industry Co., Chengdu, China. Other reagents were analytical grade and all solutions were prepared with high-purity water.

2.2. Preparation of SBCS

The synthesis of the SBCS is illustrated in Scheme 1. CS (1000mg) was dissolved in 80.0 mL of 0.2% (w/w) aqueous acetic acid solution. The solution was allowed to stand overnight, and then 4.0 mL of furfural in methanol (2:1, v/v) were slowly added. After stirring for 24 h at room temperature, the resulting mixture was washed with ethanol several times, filtered, and dried in a vacuum oven at 40 °C for 8 h. The obtained yellow powder was SB-CS.

Scheme 1.

2.3. Synthesis of *L*-Monoguluronic acid-chloride-modified

L-Monoguluronic acid (80 mg) was dispersed in 40.0 mL of thionyl chloride. The suspension was stirred for 24 h at 70 °C. The residue was separated by filtration, washed with N, N-dimethylformamide (DMF), and dried under a vacuum at 80 °C for 8 h to obtain *L*-Monoguluronic acid-COCl.

2.4. Synthesis of *GL*-SBCS

L-Monoguluronic acid-COCl (50 mg) and SBCS (400mg) were added in 30.0

mL of DMF. The mixture was stirred at 100 °C for 48 h under a nitrogen atmosphere and filtered through a 0.22- μ m microporous membrane. To remove the physically adsorbed compounds, the residue was washed with 0.2% acetic acid, ethanol, and DDW. The GL-SBCS adsorbent was obtained after drying overnight in an oven at 40 °C.

2.5. Characterization of GL-SBCS

This allows the identification of the appearance, morphology and size of the structures originated as a result of the film formation process. Microstructural analyses of the surface and section of the dry films were carried out using SEM technique in a HitachiS-3400N (Japan). The samples were cut from films and mounted in copper stubs. To allow the observation, samples were gold coated (15 nm) and observed using an accelerating voltage of 10 kV.

NMR was used in the structural identification of GL-SBCS. About 10 mg of GL-SBCS were dissolved in 1mL of CD₃COOD/D₂O(5% w/v). The temperature was kept at 333k. ¹H, with water suppression and ¹³C NMR spectra of GL-SBCS have been run at 600.13 and 150. 13 MHz, respectively, on a Bruker AMX-600 spectrometer. CS was as the control also obtain the NMR spectra used the same method.

2.6. Batch adsorption studies

Batch adsorption experiments were conducted with the GL-SBCS for the removal of CR from aqueous solutions. Equilibrium adsorption experiments were conducted by adding 0.1 g wet weight of GL-SBCS into 0.01 dm³ of the CR

solution of the desired concentration at pH 5 and at a temperature of 30 °C. All of the adsorption experiments were conducted in triplicate and performed for 24 h in shaking conditions (200 rpm). The adsorption performance of the GL-SBCS beads was studied as the function of the GL-SBCS concentration variation from 0.001 to 0.05 wt.% in the GL-SBCS beads with an initial CR concentration of 500 mg dm⁻³. The effect of a pH change was studied by changing the initial pH of the CR solutions from 4 to 9; the initial CR concentration was fixed at 500 mg/dm³. Equilibrium isotherm studies were carried out with different initial concentration of CR (10–1000 mg/dm³) at a fixed temperature (30 °C). The non-linear forms of the Langmuir, and Freundlich models were used to analyze the equilibrium adsorption isotherm data and the isotherm models were evaluated by the non-linear coefficients of determination (R^2) and a non-linear Chi-square test (χ^2). Different time intervals of up to 1500 min were used for this study. The residual CR concentration in the experimental solution (mg/dm³) was analyzed using a spectrophotometer (HACH DR-5000, USA) at a λ_{max} of 497 nm. The amount of CR adsorbed (mg/g¹) was calculated based on a mass balance equation as given below:

$$q_e = \frac{(C_0 - C_{eq}) \times V}{W} \quad (1)$$

Where q_e is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg/g; C_0 is the initial concentration of CR in the solution, mg/dm³; C_{eq} is the final or equilibrium concentration of CR in the solution, mg/dm³; V is the volume of the solution, dm³; and W is the dry weight of the hydrogel beads, g.

2.7. Influence of sodium chloride, sodium dodecyl sulphate and desorption studies

Influence of sodium chloride and sodium dodecyl sulphate on dye adsorption was studied in a similar way as described in pH experiment. Congo red solution contained either sodium chloride (0.5 M and 1M) or sodium dodecyl sulfate (1% and 2%, w/v); pH of the solution was maintained at 6.0.

After kinetic experiment, dye-loaded GL-SBCS (1g) obtained by filtration and washing with water through glass wool were taken in different 250 mL Erlenmeyer flasks. Fifty millilitres water having pH adjusted to 6-12 or 50 mL ethanol, methanol, propanol, ether, acetone was added to each flask. The flasks were agitated (50 rpm) for 24 h at 30°C and concentration of the dye in the supernatant was estimated.

3. Results and discussion

3.1 Immobilization of GL-SBCS and characterization

A comparison of the IR spectra of CS and SBCS in the synthesis process showed that a new band at 1638 cm^{-1} appeared in the SBCS spectrum. This band was attributed to the C=N stretching vibration and indicated that the Schiff base had been successfully prepared. A furan ring with a characteristic peak (δ , ppm, 7.52, 6.25, 8.22, Table 1) was shown in the SBCS' NMR spectrum, which indicated that the furfural was linked with CS through the Schiff base reaction. The carbon signal in ^{13}C -NMR also verified this reaction. A five carbon signal appears from 60~80 ppm suggesting a furan ring was present in the structure of GL-SBCS. This implies

the furfural was grafting with a Schiff base modified chitosan. Fig.1 shows the surface structure of commercial chitosan (Fig.1(a)) and grafted chitosan (Fig.1(b)). As shown in Fig.1, the chitosan surfaces are smooth, but the grafted chitosan has large pore structures, which are clearly visible. These pores might be providing sites for the location of congo red.

Fig.1 & Table 1

3.2. Adsorption of CR with GL-SBCS

After being prepared, the resultant GL-SBCS was evaluated for CR removal in aqueous solution. As shown in Fig.2A, both CS and GL-SBCS showed appreciable affinity toward CR, but the GL-SBCS gave considerably higher capacity for CR adsorption. Maximum adsorption for CR was obtained with GL-SBCS containing 60 wt% of CS. When the CS content was lower than wt%, the organic phase (SBCS) could not encapsulate all L-Monoguluronic acid, which may suggest that L-Monoguluronic acid together in an inhomogeneous way. While at a CS weight content of 50%, the L-Monoguluronic acid was almost perfectly incorporated into the composites, which enhanced the adsorption efficiency of CS for CR. However, the removal efficiency decreased slightly when CS weight content was 80 wt%, probably due to saturation of CS in the composites.

Fig.2

3.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the CR removal (400 mg/L) was evaluated in the range of 10-200 mg (Fig.2B). Generally, increasing the sorbent amount, at a

constant time, resulted in higher adsorption efficiency for CR. About 91.95% CR removal efficiency was achieved with only 40 mg of GL-SBCS, compared to more than 200 mg of CS for similar CR removal efficiency. Such results clearly demonstrate the improved CR adsorption efficiency of CS after modified through the Schiff base with furfural and encapsulation with L-Monoguluronic acid. In the following investigations, an adsorbent dosage of 40 mg was employed.

3.4. Effect of sample pH

The initial pH of the dye solution affects the chemistries of both the dye molecule and the adsorbent. In this study, the pH dependence of CR adsorption was investigated and the results were given in Fig. 2(C). Upon increasing the sample pH from 4 to 10, the CR adsorption efficiency of GL-SBCS composite, L-Monoguluronic acid and CS decreased about 5%, 20% and 30%, respectively. Besides, the CR removal efficiency of GL-SBCS composite maintained above 85% in the studied pH range. In other words the GL-SBCS composite exhibited higher immunity to pH change than L-Monoguluronic acid and CS on CR removal. In order to understand the role of pH on the adsorption process, the surface change of GL-SBCS was determined by measuring zeta potential. The surface charge of chitosan is positive in acidic pH, which decreases gradually with an increase in pH and passes through zero potential at pH 6.1. In an acidic pH range, the surface charge of the adsorbent increases mainly due to increased protonation of the amine group (-NH_3^+) of GL-SBCS. Congo red is an acidic dye and contains a negatively charged sulfonated group ($\text{-SO}_3^- \text{Na}^+$). Higher adsorption of the dye at lower pH is

probably due to the increase in electrostatic attraction between the negatively charged dye molecule and positively charged amine group of GL-SBCS. However, at pH 6.1 where surface charge of GL-SBCS hydrobeads is neutral, adsorption of the dye in this pH range may be attributed to physical forces only. The three-dimensional energy minimized structure of congo red as drawn with Chem Office 3D ultra software appears to be flat. Thus, attachment of the congo red molecule on to the surface of chitosan beads is of flat layer type. Hence, there is every possibility of hydrogen bond formation between some of the molecular components of congo red such as N, S, O, benzene ring and CH₂OH groups of the chitosan molecule. At pH above 6.4, the surface charge of chitosan beads is negative which hinders the adsorption by electrostatic force of repulsion between the negatively charged dye molecule and adsorbent (GL-SBCS); but appreciable amount of adsorption in this pH range suggests strong involvement of physical forces such as hydrogen bonding or van der Waals forces, in the adsorption process. Fig.3 represents all possible interactions between GL-SBCS and congo red.

Fig.3

3.5. Adsorption isotherm

Fig.4 shows the equilibrium adsorption of CR onto the GL-SBCS. The non-linear forms of the Langmuir and Freundlich models have been used to interpret the experiment isotherm data. The non-linearized form of the Langmuir adsorption isotherm equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where C_e is the concentration of CR in solution at equilibrium (mg/dm^3), q_e is the adsorption capacity at equilibrium (mg/g). The Langmuir constant, q_m (mg/g) is related to the maximum adsorption capacity (mg/g) of the adsorbent and K_L is the constant term related to the energy of adsorption (dm^3/mg). The maximum adsorption capacity (q_m) of the GL-SBCS for CR was 459.75 mg/g , which was the highest value among the other adsorbents reported earlier for CR adsorption (Han et al., 2008; Sudipta et al., 2010;).

A non-linear form of Freundlich equation is:

$$q_e = k_F C_e^{(1/n)} \quad (3)$$

Where k_F (dm^3/g) is the Freundlich constant related to the adsorption capacity and $1/n$ measures the surface heterogeneity. The values of k_F and $1/n$ from this isotherm model are 57.25 and 0.35 .

As shown in Fig.5, the Langmuir isotherm model showed a better fit to the experimental isotherm data than the Freundlich isotherm model. The results of the non-linear R^2 for the two adsorption isotherms indicated that the Langmuir isotherm model appeared to be the best fitting model for the adsorption isotherm data of the GL-SBCS because it displayed the highest $R^2(0.996)$ and lowest Chi-square, χ^2 value. In future work, we will study the capacity of desorption on CR from the GL-SBCS and other isotherm models.

Fig.4

3.6 Effect of contact time

Fig.5 shows the effect of contact time on the adsorption of congo red by GL-SBCS. It is apparent that the adsorption is rapid in the initial 500 min and then it becomes slow until equilibrium is reached. In the initial stage the high adsorption rate is probably due to rapid contact of congo red molecules with the active sites on the external surface of the adsorbent. The following decreased rate is firstly attributed to the diminishing availability of the remaining active sites; secondly, long-range diffusion of the dye molecules into the micropores of the adsorbent needs a relatively long time to reach equilibrium.

The contact time means the efficiency of congo red absorption in the actual wastewater treatment. Too long time could improve the cost of treatment and the dye might be desorption from the absorbent. In this study, the novel absorbent GL-SBCS contracts the CR in 500 minutes. To the extent of our knowledge, the contract time of GL-SBCS with CR was shorter than other chitosan/modified chitosan.

Fig.5

3.7. Effect of additives on adsorption and pH on desorption phenomena

Sodium slat is often used as a stimulator in dying industries and sodium dodecyl sulphate, an anionic surfactant, is often present in the effluent of dye industries; hence, their effect on the adsorption process was studied. Sodium chloride at the concentration of 0.5M and 1M reduced the dye adsorption by 15.2% and 27.4%, respectively (Fig.6). Sodium chloride is known to reduce ionic

interaction and thus this supports our posit regarding the mechanism of congo red adsorption particularly in acidic pH on the adsorbent. Sodium dodecyl sulphate like sodium chloride inhibited adsorption of congo red (Fig .6).

Investigation on the desorption of the dye from the adsorbent is necessary for its reuse and also to understand the mechanism of adsorption. Table 2 shows that the amount of dye desorbed from the loaded GL-SBCS increased with an increase in pH of the eluent. Low desorption of dye with pH change indicates that physical forces such as hydrogen bonding and van der Waals forces play the predominate role in the removal of congo red by GL-SBCS because the change in pH only affects the surface charge of the adsorbent. Organic solvents, except acetone were ineffective in the desorption of congo red from GL-SBCS. Acetone desorbed congo red but the extent was only 18%.

Fig.6 & Table 2

4. Conclusions

A novel modified chitosan adsorbent was synthesized by covalently grafting a Schiff base-chitosan (SBCS) onto the surface of L-Monoguluronic acid. The adsorbent composite with CS weight content of 60% exhibited the highest adsorption capacity for CR. The fitting of the equilibrium isotherm data of the GL-SBCS into different isotherm models showed the best fit to the Langmuir isotherm model. The maximum adsorption capacity of the GL-SBCS obtained from the Langmuir model was 459.75 mg/g. Thus, GL-SBCS impregnation may be a good method to enhance adsorption capacity and the mass transfer rate of chitosan

hydrogel beads, as well as their mechanical strength.

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Tables

Table 1. The NMR data of CS and GL-SBCS

	¹ H-NMR	¹³ C-NMR
1	1.46	37.2
2	3.21	67.2
3	1.06	55.7
4	2.96	71.2
5	1.94	27.6
6	1.22	31.5
7	4.22; 4.19	68.5
8	7.66	165.2
1'	7.92	143.5
2'	6.56	113.7
3'	6.88	119.2
4'	/	152.7
1a	4.87	81.5
2a	4.96	73.6
3a	3.81	76.8
4a	3.87	72.4
5a	5.77	98.2
6a	/	172.5

Table 2. Desorption of congo red from GL-SBCS

pH	% of dye desorbed
6.0	10.7
7.0	12.1
8.0	14.6
9.0	16.7
10.0	18.5
11.0	21.5
12.0	25.2

Figure captions

Scheme 1. Synthesis and structure of GL-SBCS.

Fig.1 SEM characterization of chitosan (a) and GL-SBCS(b).

Fig.2 Adsorption experiments: (A) Effect of CS weight content in GL-SBCS composite on the removal of CR. (B) Effect of adsorbent dosage on removal of CR by CS, GL and GL-SBCS. (C) Effect of the initial pH values on removal of CR by CS, GL and GL-SBCS.

Fig.3 Congo red–chitosan interaction: (a) ionic interaction (involves when pH of experimental solution is below 6.4), (b) hydrogen bonding between hydroxyl group of GL and electronegative residues in the dye molecule, and (c) Yosida H- bonding between hydroxyl group of A-SBCS and aromatic residue in dye.

Fig.4 Plots of q_e vs. C_e for the adsorption of CR onto the GL-SBCS; pH 5 and 30 °C.

Fig.5 Effect of contract time on the adsorption of congo red onto GL-SBCS.

Fig.6 Effect of sodium chloride and sodium dodecyl sulphate over the adsorption of congo red by GL-SBCS.

Scheme 1.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6