Removal of Hazardous Food Dye, Brilliant Blue Fcf from Aqueous Solution by Magnetic Crosslinked Chitosan Beads

Zararlı Bir Gıda Boyası olan Brilliant Blue Fcf'nin Sulu Ortamdan Çapraz Bağlı Manyetik Kitosan Boncuklar ile Giderimi

Research Article

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ABSTRACT

The use of magnetic crosslinked chitosan beads for the removal of hazardous dye "Brilliant Blue FCF" from aqueous solution at different initial pH levels, contact times and initial concentrations was studied. The equilibrium adsorption data were described by Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms. The experimental results showed that the maximum adsorption of dye pH was 2.0. Equilibrium was attained in 150 min. The equilibrium sorption was best described by the Dubinin-Radushkevich adsorption isotherm model. The estimated values of E for the present study were found to be >8kj/mol at room temperature which implies that adsorption of Brilliant Blue FCF onto magnetic crosslinked chitosan beads is chemisorption. The study indicates that dye adsorption onto chitosan beads is becoming an alternative replacement for the conventional adsorbents used for dye removal purposes. Also, as they are magnetic it is easy to separate the beads from the water after the treatment.

Key Words
Brilliant Blue FCF, Food Dye Removal, Waste Water Treatment, Chitosan, Magnetic Beads, Crosslinked Chitosan

ÖZET

Çapraz bağlı manyetik kitosan boncuklar ile, zararlı bir boya olan "Brilliant Blue FCF" nin sulu ortamdan farklı pH seviyeleri, etkileşim süreleri ve konsantrasyonlarda adsorpsiyonu çalışılmıştır. Boyanın ortamdan adsorpsiyon sabitleri Langmiur, Freundlich ve Dubinin-Radushkevich adsorpsiyon izotermlerine göre açıklanmıştır. Deneysel verilere gore, boyanın maksimum adsorplandığı pH değeri 2.0' dir. Adsopsiyon ortamı 150 dakikada dengeye gelmiştir. Boyanın ortamdaki adsorpsiyonu en iyi Dubinin-Radushkevich adsorpsiyon izoterm modeli ile açıklanmıştır. Yapılan çalışmada E değeri > 8 kj/mol olarak bulunmuştur ve bu sonuç Brilliant Blue FCF'nin çapraz bağlı manyetik kitosan boncuklar üzerine kemisorpsiyon ile bağlandığını göstermektedir. Yapılan çalışma, kitosan boncuklar üzerine boya adsopsiyonunun, kullanılan geleneksel adsorbanların yerine boya giderimi amacıyla kullanılabilecek bir alternatif olduğuna işaret etmektedir. Ayrıca boncukların, manyetik özelliği sayesinde uygulama sonrasında ortamdan kolaylıkla ayrılmaları da mümkün olabilecektir.

Anahtar Kelimeler
Brilliant Blue FCF, Gıda Boyası Giderimi, Atık Su Arıtımı, Kitosan, Manyetik Boncuklar, Çapraz Bağlı Kitosan

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INTRODUCTION

Dyes are widely used in many industries such as food, textiles, rubber, paper, plastics and so on. About over 7.105 to 10.000 different commercial dyes and pigments are produced annually all around the world. It has been estimated that about 10-15% of these dyes is lost during the dyeing process and released with the effluent [1]. The discharging of these dyes into water resources even in small amounts can affect aquatic life and the food chain. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms [2].

The Brilliant Blue molecule is a weak acid organic molecule with polar and non-polar components, which may lead to complex sorption behavior. Its negative charge stems from sulfonic acid groups [3]. It is used as a common food additive to color confectionary and dairy products. It is carcinogenic, causes reproductive and neurological disorders, severe allergies, anaphylactic reactions including rashes, swelling and trouble in breathing in human being. Even behavioral convulsion, gastrointestinal tumors, blood-lymphoma have also been found in rodents [4]. Very few techniques for the removal of Brilliant Blue FCF from industrial waste water have been studied because of its complex structure. Reports exist on the removal of this dye through electrochemical, photochemical and adsorption [5].

Chitin, found in the exoskeleton of crustaceans, the cuticles of insects, and the cells walls of fungi, is the most abundant amino-polysaccharide in nature. Since the biodegradation of chitin is very slow in crustacean shell waste, the accumulation of large quantities of waste from the processing of crustaceans has become a major concern in the seafood processing industry. So, there is a need to recycle these byproducts. Their use for the treatment of wastewater from other industries could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy. More important than chitin is its derivative, chitosan [6].

Chitosan is a polysaccharide usually obtained from deacetylation of chitin, which after cellulose is the second most abundant natural biopolymer found in nature [5]. It is being used as an attractive source of adsorbents. Besides being natural and plentiful, chitosan possesses interesting characteristics that also make it an effective adsorbent for the removal of dye as it has outstanding adsorption capacities. Three factors have specifically contributed to the growing recognition of chitosan as a suitable biomaterial for dye removal [5].

1- Chitosan based polymers are low-cost materials. In many countries, fishery wastes are used as excellent sources of chitosan.

2- High adsorption capacities have been reported.

3- It can be manufactured in the form of films, membranes, fibers, sponges, gels, beads and nano-particles, or supported on inert materials.

Chemical modifications increase the sorption in strong acids and improve the mechanical strength of chitosan. Some of the chemical modifications may include cross-linking using a cross-linking agent. Some of the most commonly used cross-linking agents are glutaraldehyde, epichlorohydrine and ethylene glycoldigliycidyl ether [7].

In this study magnetic crosslinked chitosan beads were prepared. The adsorption behavior of Brilliant Blue FCF was studied in a batch reactor within various adsorption parameters, including pH, dye concentration and contact time, so that the adsorption process could be optimized. The dye adsorption isotherms, Langmiur, Freundlich and Dubinin-Radushkevich (D-R) were calculated.

MATERIALS AND METHODS

Chitosan was purchased from the Sigma Chemical Company and the Brilliant Blue FCF was a purchased food product. All the reagents were analytical grade.

Preparation of Chitosan Beads

The chitosan solution was prepared by dissolving 1, 1.5 and 2% chitosan into a 5% acetic acid solution. The chitosan solution was added dropwise to a 1 M NaOH solution with a syringe, resulting in the formation of chitosan beads. After 4h of incubation, these were separated by filtration and washed with distilled water. The magnetic chitosan beads were prepared using the same procedure. Barium ferrite was used for its magnetic properties. Barium ferrite (10-100 mg) was added to the chitosan solution. It was dispersed via ultrasound. The Barium ferrite-chitosan solution was added dropwise to a 1 M NaOH solution, and after 4h of incubation these were separated by filtration and washed three times with distilled water. Magnetic chitosan beads were incubated for 1h with 2% glutaraldehyde in order to prepare the crosslinked magnetic chitosan beads. After incubation the beads were washed several times with distilled water. The particle size of the beads was determined with the aid of a magnifying glass. This was roughly checked by suspending the beads in water contained in 10 mL of graduated cylinder and measuring the volume.

Adsorption Studies

The adsorption process was monitored at room temperature (25^{o}C). The magnetic crosslinked chitosan beads were used for the removal of the Brilliant Blue FCF. The effects of pH, contact time and dye concentration were investigated. The initial pH of the solution was altered between 1.0 and 6.5 by the addition of either HCl or NaOH. To calculate the concentration of the sample from each experiment a calibration curve of dye was prepared first. The absorbance was measured using a Perkin Elmer UV/VIS Spectrophotometer yielding a maximum absorption rate of 629 nm.

Adsorption Equilibrium Isotherm

In order to determine the adsorption potential an adsorption isotherm is essential. These equilibrium adsorption capacity curves can be obtained by measuring the adsorption isotherm of Brilliant Blue FCF onto the adsorbent. Three isotherm equations including Langmiur, Freundlich and D-R were used in this study.

RESULTS AND DISCUSSION

Preparation of Beads

The sphere-shaped magnetic crosslinked chitosan beads instantly formed in the NaOH solution when the chitosan solution was added dropwise to a 1 M NaOH solution with a syringe. Among the prepared chitosan solutions used, the 1.5% chitosan solution had the most appropriate viscosity for forming sphere-shaped chitosan beads via the dropping method. Therefore, we used a 1.5% chitosan solution to prepare chitosan beads.

The particle size of the beads was determined with the help of a magnifying glass. The size of the magnetic chitosan particles varied in direct proportion to the amount of Barium ferrite. Thus, the size and shape of the magnetic chitosan beads depended on the amount of Barium ferrite. The average diameter for the magnetic beads was found to be 200 μm when used 20 mg Barium ferrite and 250 μm when used 30 mg Barium ferrite. If over 30 mg Barium ferrite was used the beads were not formed properly so 20 mg of Barium ferrite amount was chosen for the preparation of the magnetic beads.

The concentrations of the Brilliant Blue FCF samples can be calculated with equation, $y = 0.1656x$, $R^2 = 0.9996$, obtained by standard curve.

Effect of Initial pH

The pH of the dye solution plays an important role in the whole adsorption process in particular on the adsorption capacity. The pH level affects the surface charge of the adsorbent. Chitosan is a weak base and is insoluble in water and organic solvents. It is soluble in a dilute aqueous acidic solution (pH < 6.5) which can convert the glucosamine units into a soluble from $-NH_3^+$. Chitosan is polycationic in an acidic medium; the free amino groups are protonated and the polymer becomes fully soluble and this facilitates electrostatic interaction between chitosan and the negatively charged anionic dyes [5].

In this study the pH level for Brilliant Blue FCF adsorption ranged between pH 1.0-6.5.

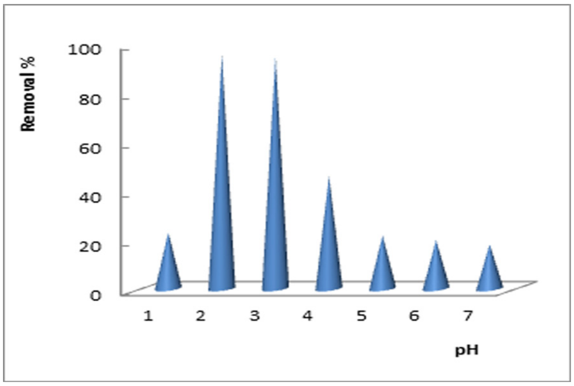

Figure 1. pH effect on adsorption.

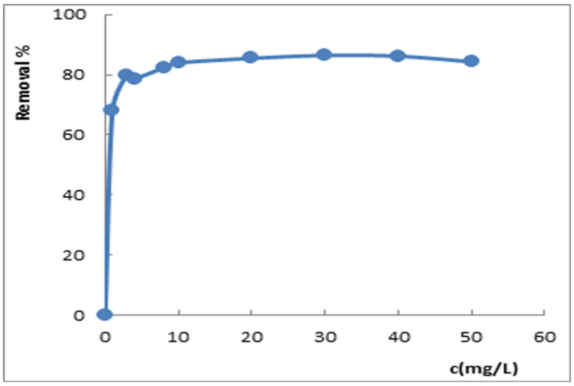

Figure 2. Effect of dye concentration on adsorption

Figure 1 shows the adsorption capacity of magnetic crosslinked chitosan beads. As seen from Figure 1, it is observed that the adsorption capacity of dye onto chitosan beads increased with a decrease in the initial pH value of the solution. The maximum adsorption of dye onto beads occurred at the pH 2.0. At lower pH, the adsorption capacity of beads was high because chitosan has a positively charged surface. In a lower pH solution more protons will be available to protonate the amino groups of chitosan molecules in order to form $-NH_3^+$ groups. This increases the electrostatic attraction between the anionic group ($-SO_3^-$) of the dye and protonated amino groups (NH_3^+) of chitosan causing an increase in dye adsorption. However, the lower dye adsorption within a higher pH solution may be due to the abundance of hydroxide ions (OH^-) and the ionic repulsion occurring between the anionic dye molecules and the negatively charged surface of the chitosan. The optimum pH is frequently reported in the literature to be around pH acidic medium for anionic dye adsorption [5, 8, 9].

Effect of Initial Dye Concentration

Figure 2 depicts the curve for the adsorption of dye onto beads at different initial dye concentrations. As is shown in Figure 2, the amount of the dye adsorbed onto beads increased as the concentration of dye solution increased, provided the amount of adsorbent was kept unchanged. This is due to the increase in the driving force of the concentration. Over 10 mg/L dye concentration the adsorption capacities were about stable. Hence, 10 mg/L dye concentration was chosen as the optimum dye concentration.

Effect of Contact Time

Contact time is important variable in adsorption of dye. During the process the adsorbent surface is progressively blocked by the adsorbate molecules, becoming saturated after some time. When this

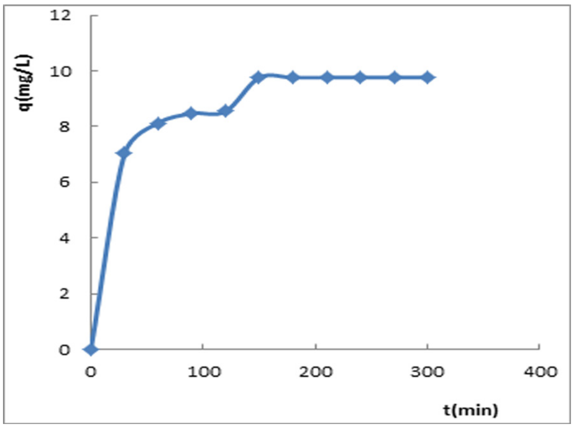

Figure 3. Effect of contact time on adsorption

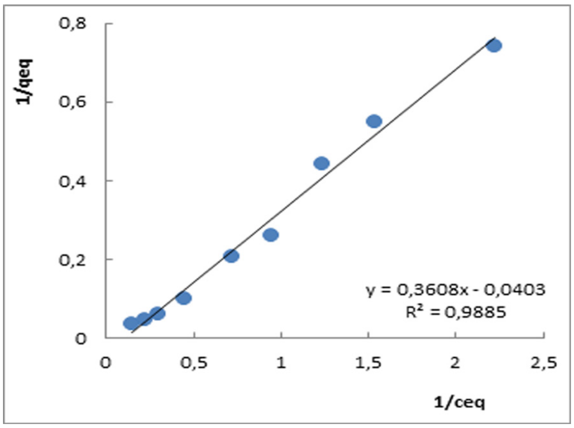

Figure 4. Langmiur ısotherm.

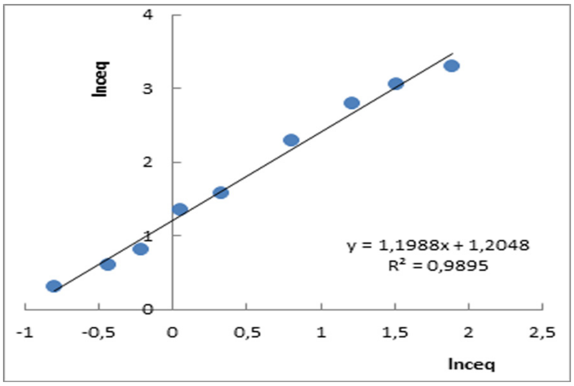

Figure 5. Freundlich ısotherm.

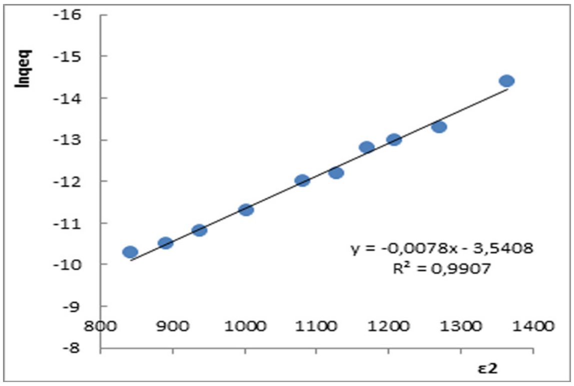

Figure 6. Dubinin-Radushkevich ısotherm.

happens, the adsorbent can no longer adsorb any more dye molecules [5]. Figure 3 shows the effects of contact time on the amount of dye adsorbed onto magnetic crosslinked chitosan beads under optimum conditions (pH 2.0, dye concentration 10 mg/L). As is shown in Figure 3, the adsorption of dye onto beads is rapid at first. It then gradually slows down before finally reaching the equilibrium. In this system nearly 100% of the adsorption occurred within 150 min.

Adsorption Isotherms

The adsorption isotherms of the Brilliant Blue FCF onto beads were obtained for pH 2.0 at room temperature for 150 min with different dye concentrations. There are several isotherm models available for analyzing experimental data and for describing the equilibrium of adsorption, including Langmuir, Freundlich and Dubinin-Radushkevich, BET, Toth, Temkin, Redlich-Peterson, Sips, Frumkin, Harkins-Jura, Halsey and Henderson isotherm [5]. In this study Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were used.

Langmuir's model of adsorption predicts the existence of monolayer coverage of the adsorbate across the outer surface of the adsorbant. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent, which implies that all adsorption sites are identical and energetically equivalent [10]. The linear form of the Langmuir isotherm is expressed as;

$$C_{eq}/q_{eq} = 1/Q_o \text{ x } b + c_{eq}/Q_o$$

where q_{eq} is the amount of dye adsorbed per unit weight of adsorbent (mg/g) and C_{eq} is the equilibrium concentration of dye in solution (mg/L). The constant Q_o signifies the adsorption capacity (mg/g) and b is related to the energy of the adsorption (L/mg).

A plot of $1/q_{eq}$ versus $1/c_{eq}$ yields a straight line with slope $1/b.Q_o$ and intercept $1/Q_o$. The modeled adsorption isotherm was plotted in Figure 4. As is shown in Figure 4 the linear form was not investi-

Table 1. Freundlich and Dubinin-Radushkevich isotherm model constants and correlation coefficients for adsorption of Brilliant Blue FCF.

	Freundlich	Dubinin-Radushkevich
n	12.9026	-
K_F	212.9160	-
q_m	-	0.029
β	-	0.0078
E	-	8.0064
R^2	0.9895	0.9907

gated so the Langmuir isotherm model is not available for describing the equilibrium of adsorption in this study.

The Freundlich isotherm is an empirical equation based on a heterogeneous surface. A linear form of the Freundlich expression will yield the constants K_F and n [10]. Hence,

$$\ln q_{eq} = \ln K_f + (1/n \times \ln C_{eq})$$

Therefore, a plot of $\ln q_{eq}$ versus $\ln C_{eq}$ enables the constant K_F and exponent n to be determined (Figure 5).

Parameters of the Freundlich were computed in Table 1. The slope 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. This value was determined to be 1,199.

The D-R model is based on the heterogeneous characteristics of adsorbent and is expressed as;

$$\ln q_{eq} = \ln q_m - \beta \varepsilon^2$$

$$\varepsilon = RT\ln(1 + \frac{1}{ceq}$$

Where qm is the theoretical saturation capacity, βis a constant related to the biosorption energy, γ is the Polanyi potential, R is the universal gas constant (8.314 j/mol.K) and T is the absolute temperature. The values of q_m and βare obtained by plotting $\ln q_{eq}$ versus γ^2 [11, 12]. Figure 6 showed the adsorption isotherms of the dyes at pH 4.0 and room temperature with different equilibrium dye concentrations. The parameters of the D-R model were computed in Table 1.

The D-R isotherm model constant β gives an idea about the mean free energy E (kj/mol) of biosorption per mole of the adsorbate, which in turn can give information about the type of sorption mechanism. E can be calculated using the relationship:

$$E = \frac{1}{\sqrt{-2\beta}}$$

It is known that magnitude of apparent energy E is useful for estimating the type of adsorption and if this value is below 8kj/mol the adsorption type can be explained by physical adsorption; if it is between 8 and 16 kj/mol the adsorption type can be explained by ion exchange, and at values over 16 kj/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange [13, 14]. The estimated values of E for the present study were found to be >8 kj/mol, which implies that adsorption of Brilliant Blue FCF onto magnetic crosslinked chitosan beads is chemisorption.

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