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Research Article

Congo Red Biosorption with Dried Mint Leaves; Isotherm and Kinetic Studies

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Abstract

The development of the industry has resulted in a proportional increase in waste materials. Waste industrial products play a major role in the pollution of nature along with seas, lakes, and various water resources around the world. Organic dyes, which do not degrade in nature and have carcinogenic effects, are important industrial wastes. The improvement of wastewater is a research topic that has gained importance in recent years. In this study, the biosorption of Congo red dye from aqueous solution with dried mint leaves was investigated. The experiments were carried out at 20 °C and the natural pH of the dye. The process was optimized by examining the parameters of initial dye concentration, amount of biosorbent and contact time. It was determined that the biosorption equilibrium conformed to the Langmuir isotherm (R^2=0.9815) and the maximum biosorption capacity (q_{max}) was 60.24 mg/g. In addition, the process conforms to the pseudo-second-order (R^2=0.9946) kinetic model. As a result of the process, the removal of the Congo red dye from the dried mint leaves from the aqueous solution was achieved at a level of approximately 70%.

Keywords: Mint, Biosorption, Congo red, Isotherm, Dye.

Kurutulmuş Nane Yaprakları ile Kongo Kırmızısı Biyosorpsiyonu; İzoterm ve Kinetik Çalışmalar

Öz

Sanayinin gelişmesi, atık maddeler ile orantılı olarak bir artışa neden olmuştur. Atık sanayi ürünleri, dünya genelinde denizler, göller ve çeşitli su kaynakları ile birlikte doğanın kirlenmesinde büyük rol oynamaktadır. Doğada bozulmayan ve kanserojen etkileri olan organik boyalar önemli endüstriyel atıklardır. Atıksuyun iyileştirilmesi son yıllarda önem kazanan bir araştırma konusudur. Bu çalışmada, kurutulmuş nane yaprakları ile sulu çözeltiden Kongo kırmızısı boyasının biyosorpsiyonu araştırılmıştır. Deneyler 20 °C'de ve boyanın doğal pH'ında gerçekleştirilmiştir. Proses, başlangıç boya konsantrasyonu, biyosorbent miktarı ve temas süresi parametreleri incelenerek optimize edilmiştir. Biyosorpsiyon dengesinin Langmuir izotermine (R^2=0.9815) uygun olduğu ve maksimum biyosorpsiyon kapasitesinin (q_{max}) 60.24 mg/g olduğu belirlendi. Ek olarak, proses sözde ikinci dereceden (R^2=0.9946) kinetik modele uygundur. Proses sonucunda sulu çözeltiden kurutulmuş nane yapraklarından Kongo kırmızısı boyasının uzaklaştırılması yaklaşık %70 düzeyinde sağlanmıştır.

Anahtar Kelimeler: Nane, Biyosorpsiyon, Kongo kırmızısı, İzoterm, Boya.

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1. Introduction

With the developing industry, organic dye wastes in the aquatic ecosystem are seriously harmful due to their toxic and carcinogenic properties [1]. Some dyes with carcinogenic and mutagenic properties can affect the brain, kidney, liver, excretory and respiratory system or nervous system. This can lead to serious health problems [2]. Various methods such as adsorption, electrocoagulation, ion-exchange, ultrasound irradiation or biodegradation are used to remove dyestuffs from water. Adsorption is a simple, inexpensive and easily applied method. A diazo dye with an amine group in its structure, Congo red is utilized in a variety of sectors including paper and textiles [3,4].

Many different material groups can be used for adsorption. Materials with different properties and structures such as metal oxides, carbon-based materials such as graphene, hydrogels, polymer reinforced composites or aerogels are selected as adsorbent [2][5][6]. However, various natural materials such as plants, bacteria or agricultural wastes are also used as biosorbent. These biosorbents are both easy to obtain and inexpensive [7]. In this study, mint leaves were chosen as biosorbent.

In this study, removal of Congo red dye from aqueous solution was studied by biosorption of dried mint leaves. The effects of initial dye concentration, amount of biosorbent and contact time on biosorption were investigated. The equilibrium and structure of the biosorption process were investigated by Langmuir, Freundlich and Temkin isotherms and pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and Intraparticle diffusion kinetic models.

2. Material and Method

The mint leaves used as biosorbent were obtained from the local markets Congo red from the Harleco Company. Mint leaves were left to dry on their own at room temperature. It was then crushed by hand. Congo red dye was prepared as 1000 mg/L stock solution. In order to reduce the margin of error, other solutions were prepared by dilution from this solution and used. In the study, experiments were carried out with a batch system and a dye volume of 100 mL. The biosorption process was examined for 240 minutes by adding certain amounts of mint leaves to the dye solution. Samples taken from the suspension at certain times were filtered. Absorbance measurements were made in UV/Vis spectroscopy at 497 nm, the maximum absorbance wavelength of Congo red. All experiments were performed at room temperature at 20°C. Some properties of Congo red are given in Table 1.

Table 1. Physical and chemical properties of dye

Dye	Congo red
Chemical formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Ionic structure	anionic
Color	Blue-red
λ_{max}	497 nm
Molecule weight (g/mol)	697

Biosorption efficiency and biosorption capacity values (q) were calculated according to Equations 1, 2 and 3.

$$Biosorption\ efficiency(\%) = \left(\frac{Co-C}{Co}\right) * 100 \quad (1)$$

$$qe = \frac{(Co-Ce).V}{m} \quad (2)$$

$$qt = \frac{(Co-Ct).V}{m} \quad (3)$$

Here C (mg/L) denotes the dye concentration. Co is the initial dye concentration, Ct is the dye concentration at time t. qe is the biosorption capacity (mg/g) at equilibrium, qt is the biosorption capacity (mg/g) at t. V is the dye volume (mL) and m is the amount (g) of biosorbent.

3. Results and Discussion

Congo red was used as a model dye compound in this work, and the biosorption process of dried mint leaves was examined by optimizing the initial dye concentration (10-250 mg/L), the amount of biosorbent (1-10 g/L), and the contact time (0-240 min). In Fig. 1, graphs of variation of biosorption efficiency and biosorption capacity according to different parameters are given. Fig. 1a, the biosorption capacity increased with the increase of the initial dye concentration, but the biosorption efficiency decreased. This may be due to the saturation of the biosorbent surface at high dye concentrations [8]. The interaction between the concentration of the dye and the accessible pores on an adsorbent surface determines the effect of initial dye concentration [9]. According to Figure 1a, the concentration with the highest biosorption efficiency is 25 mg/L. While examining the effect of the amount of biosorbent in Figure 1b, the initial concentration was kept constant as 25 mg/L. While the amount of biosorbent was 0.5 g/L, the biosorbent efficiency (%70.34) reached its highest value. The aglomeration of the biosorbent may be the cause of the decline in biosorption capacity as the amount of biosorbent rises [8]. In Fig. 1c, it is seen that the biosorption efficiency and biosorption capacity increase linearly in the first 15 minutes, and then the rate slows down.

Equation 4 represents the Langmuir isotherm. Here, qmax is the maximum adsorption capacity and K_L is the isotherm constant. The value of R_L given in Equation 5 is again the Langmuir isotherm constant and gives an idea about the suitability of the isotherm. The isotherm is unfavorable if R_L exceeds 1 and favorable if it is between 0 and 1 and irreversible if it is equal to 0. Equation 6 expresses the Freundlich isotherm, K_f and is the isotherm constant. If is between 0 and 1, the isotherm is suitable. Equation 7 formulates the Temkin isotherm. B_T and K_T are related constants.

$$\frac{1}{qe} = \frac{1}{qmax} + \left(\frac{1}{K_L.qmax}\right)\left(\frac{1}{Ce}\right) \quad (4)$$

$$R_L = \frac{1}{1+KL.Co} \quad (5)$$

$$Lnqe = LnKf + \left(\frac{1}{n}\right) LnCe \quad (6)$$

$$qe = B_T\, LnK_T + B_T LnCe \quad (7)$$

In Figure 2 a, b and c, there are graphs of Langmuir, Freundlich and Temkin isotherm models, respectively. When the graphs are examined, it is seen that the highest regression value (R^2=0.9815) belongs to the Langmuir isotherm. This result shows us that the biosorption is monolayer and has a homogeneous surface [1]. The qmax value was calculated as 60.24 mg/g and the K_L constant as 0.0095 L/mg. The R_L value is calculated as 0.42, which means that the isotherm is favourable.

Examination of biosorption kinetics was maintained at an initial dye concentration of 25 mg/L, a biosorbent amount of 0.5 g/L, and a contact time of 240 minutes. Equation 8 defines PFO model, Equation 9 defines PSO, Equation 10 Intraparticle diffusion and Equation 11 define Elovich kinetic model. Respectively, k_1 is the PFO model, k_2 is the PSO model, k_i is the intraparticle diffusion model, and α and β are the reaction constants over the Elovich model.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303}t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2.q_e 2} + \frac{1}{q_e}t \quad (9)$$

$$q_t = k_{id}.t^{1/2} + C \quad (10)$$

$$q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln t \quad (11)$$

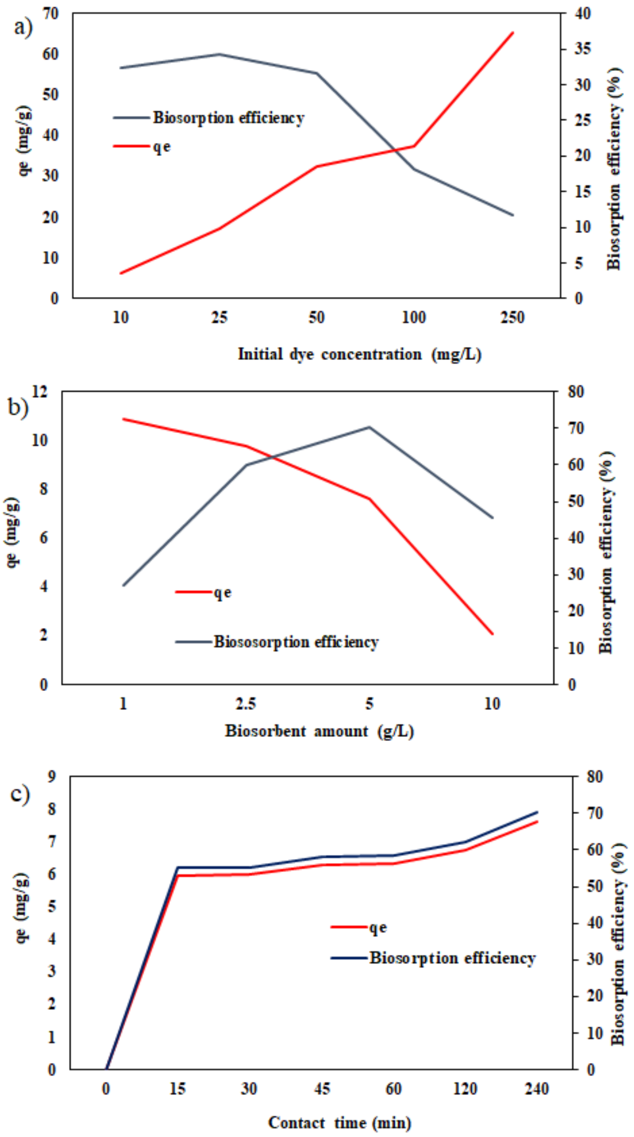

Fig 1. Graphs of biosorption efficiency and biosorption capacity for different parameters, a) Initial dye concentration, b) biosorbent amount, c) contact time

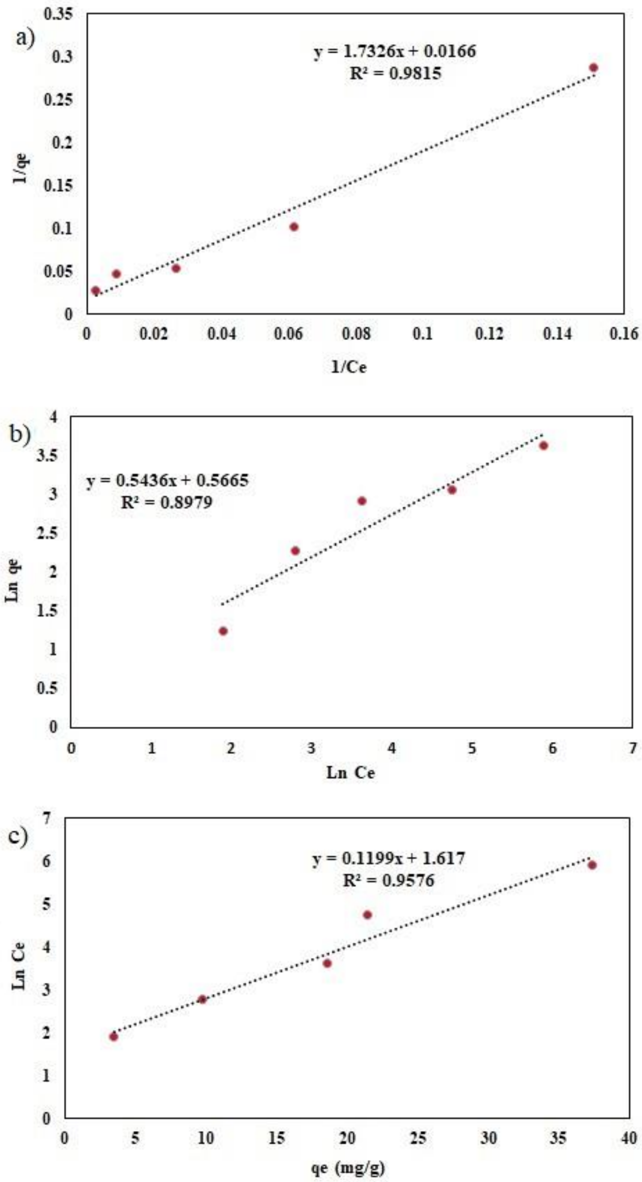

Fig 2. Isotherms a) Langmuir, b) Freundlich and c) Temkin

Biosorption kinetics are important for studying the structure and equilibrium data of biosorption [2]. When Figure 3 is examined, it is seen that the highest regression value (R^2=0.9946) is suitable for the PSO model. Compliance with the PSO model indicates that chemical adsorption takes place in the biosorption process [9]. The rate constant k_2 value of the PSO model was calculated as 0.017 g/mg.min The regression value (R^2) for PFO was determined as 0.3, for intraparticle diffusion 0.6247 and for the Elovich model 0.8957.

Color changes of mint leaves before and after biosorption are given in Fig. 4a and b. Since the color of the natural pH value of Congo red is red, mint leaves were dyed red at the end of 240 mins. This result indicates that the mint leaves adsorbed the dye on its surface.

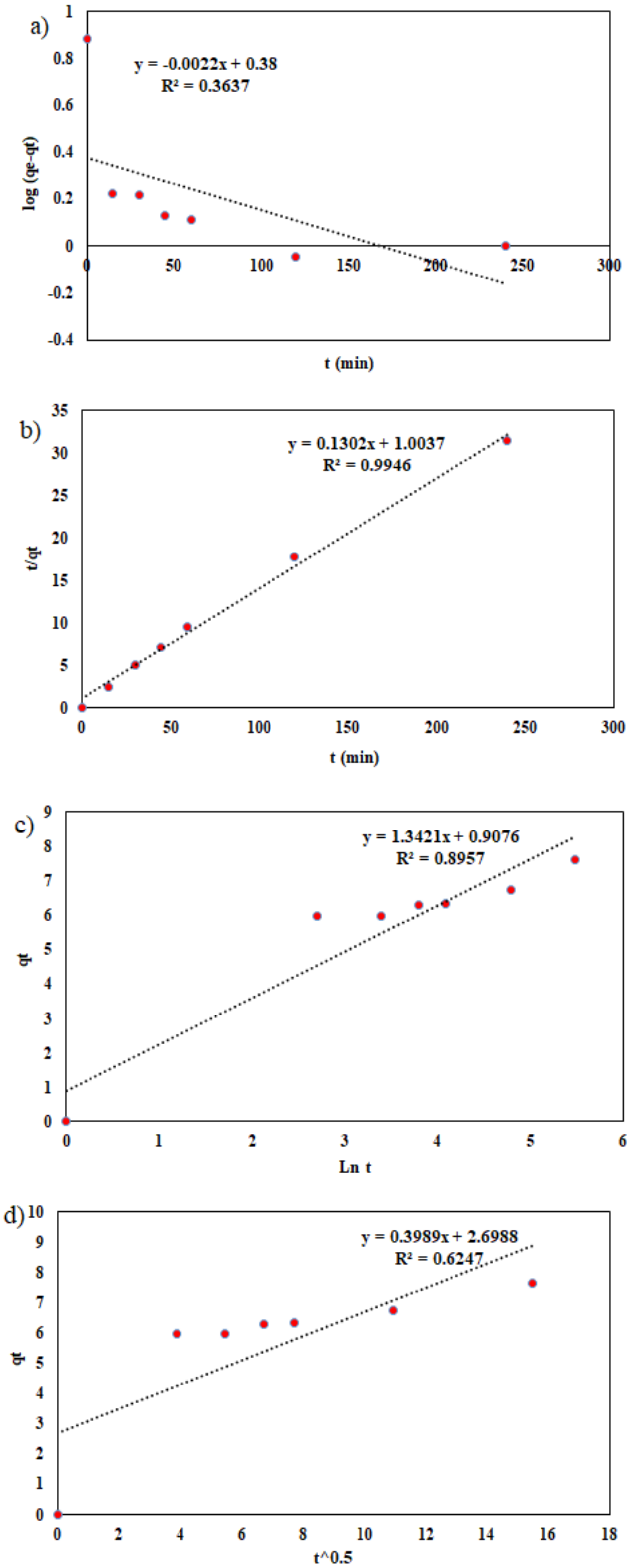

Fig 3. Kinetics models a) PFO, b) PSO, c) Elovich, d) Intra particle diffusion

The possible biosorption mechanism of mint leaves to Congo red dye is monolayer biosorption according to the results of the data. It was determined that there was chemical adsorption according to PSO on the surface of the biosorbent, which was determined to have a homogeneous surface. These results were determined at the natural pH of the dye itself. These results may vary for acidic or basic media.

Fig 4. Unloaded mint leaves, b) Loaded mint leaves

4. Conclusions and Recommendations

In this study, dried mint leaves were used as biosorbent and Congo red anionic dye was removed from the aqueous solution. The initial dye concentration was 25 mg/L, the biosorbent amount was 5 g/L, and the biosorption efficiency was 70% at the end of the 240 min contact time. Studies were carried out at the natural pH of the dye. The process of biosorption was determined to fit the Langmuir isotherm and pseudo-second-order reaction kinetics model. The qmax value was calculated as 60.24 mg/g. As a result of this study, it was concluded that mint leaves can be used as a biosorbent. It can be used to protect the ecological system by means of biosorption by growing at the waterside where industrial wastes are found.

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