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Research Article

Nonlinear Regression Analysis of the Adsorption of Basic Green-5 from Aqueous Solutions onto a Low-Cost Biodegradable Adsorbent Material

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Abstract

Industrial wastewater containing dyes is a main reason for the pollution of water resources. These dyes are toxic and may threaten ecosystems and the human health and they are resistant to sunlight and to high temperature. Worldwide production of dyes in textile, leather, pharmaceuticals and other large industries such as food, constitutes 10,000 different dyes and pigments with an amount of 8×10^5 tons annually. Nowadays, several physical and chemical methods and technologies are used for the purification process of wastewater before it is discharged to the environment, moreover these methods can be improved. In this study, removal of basic green-5 dye from aqueous solutions by calcined eggshell (ES) through the adsorption process is analyzed. The experiments were carried out at 25, 35, 45 oC. Experiments were carried out for four different initial concentration values of the dye. Also, surface fitting plots were created to show the effect of the amount of the eggshell waste, pH and temperature on adsorption. BET surface area and SEM analyzes were performed for calcined ESs. Non-linear regression analysis was applied for Baudu and Fritz-Schlunder Isotherms. Results obtained show that the calcined ES can be a convenient, cost-effective alternative for this adsorption.

Keywords: Adsorption, Basic Green-5 Dye (BG5), Biodegradable adsorbent, Calcined eggshell, Non-linear adsorption isotherm.

Bazik Yeşil-5'in Sulu Çözeltilerden Düşük Maliyetli Biyobozunur Bir Adsorban ile Adsorpsiyonunun Doğrusal Olmayan Regresyon Analizi

Öz

Boya içeren endüstriyel atık sular, su kaynaklarının kirlenmesinin ana nedenidir. Bu boyalar toksik olup, ekosistemleri ve insan sağlığını tehdit edebilirler. Ayrıca, güneş ışığına ve yüksek sıcaklığa dayanıklıdır. Tekstil, deri, ilaç ve gıda gibi büyük endüstrilerdeki boyaların dünya çapında üretim miktarı, yıllık 8×10^5ton olup, 10.000 farklı tür boya ve pigmentten oluşmaktadır. Günümüzde atıksuların çevreye deşarj edilmeden önce kirlilikten arındırılması için çeşitli fiziksel ve kimyasal yöntem ve teknolojiler kullanılmaktadır, ayrıca bu yöntemler geliştirilebilirler. Bu çalışmada, kalsine yumurta kabuğu (YK) ile sulu çözeltilerden basic green-5 boyasının adsorpsiyon işlemi ile uzaklaştırılması araştırılmıştır. Deneyler 25, 35, 45^{o}C'de gerçekleştirilmiştir. Boyanın dört farklı başlangıç konsantrasyonu için deneyler yapılmıştır. Ayrıca yumurta kabuğu miktarı, pH ve sıcaklığın adsorpsiyon üzerindeki etkisini göstermek için yüzey uydurma grafikleri oluşturulmuştur. Kalsine edilen YK'ları için BET yüzey alanı ve SEM analizleri yapılmıştır. Baudu ve Fritz-Schlunder İzotermleri için doğrusal olmayan regresyon analizi uygulanmıştır. Elde edilen sonuçlar, kalsine YK'nun bu adsorpsiyon için iyi ve ucuz bir alternatif olarak kabul edilebileceğini göstermektedir.

Anahtar Kelimeler: Adsopsiyon, Bazik yeşil-5, Biyobozunur adsorban, Kalsine yumurta kabuğu, Doğrusal olmaya adsorpsiyon isotermleri.

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1. Introduction

High and adequate quality water is indispensable for all living beings. Nowadays water pollution has become a serious issue (Borhade and Kale, 2017). A large amount of coloured wastewater is generated from coloured components called dyes. Dyes are anionic, cationic or non-ionic compounds that are widely used in the industry e.g. textiles, printing, rubber, cosmetics, plastics, leather, etc to colour the products. (Vital et al., 2016). The first synthetic dye Mauve (Mauveine) was invented by Perkin in 1856. Since then, more than 100,000 dyestuffs have been commercially produced. Nowadays, more than 1,000,000 tons of paint are produced per year. 50% of these are textile dyes (Singh and Arora, 2011).

Various methods like coagulation-flocculation, adsorption, membrane technology, ion-exchange, irradiation are used for the removal of these dyes from water (Singh and Arora, 2011), Fenton reagent methods, ozonation, photocatalyst, degradation (aerobic or anaerobic), electrokinetic and others (Dawood and Sen, 2014). To remove the organic pollutants dissolved in water, adsorption is an effective and frequently used treatment procedure. Because of the initial investment costs, ease of operation, simplicity of design and its insensitivity to toxic substances, adsorption is known to be a superior technique, compared to other techniques available for wastewater treatment (Vital et al., 2016; Singh and Arora, 2011, Dawood and Sen, 2014).

Tran et al., (2017) investigated adsorption of basic green 5 (BG5) with activated carbon synthesized from golden shower through a new chemical activation process. BG5 was also tested with three different adsorbents, activated clay, mont-morillonite, and activated carbon (Shiau and Pan, 2005). The dynamic data indicate that activated carbon was suitable for BG5. Ghaedi et al., (2014) investigated sorption of BG5 from aqueous solution using Ag and ZnO nanostructures loaded on activated carbon.

The eggshell is one of the most generic biomaterials in nature, but unfortunately after the removal of the inner contents of the cracked egg are further utilised, the waste eggshell is often simply discarded (Baláz et al., 2016). Eggshells, considered a hazardous waste by EU (European Union) regulations, are discarded, amounting hundreds of thousands of tones worldwide (Laca et al., 2017). The eggshell waste is made up of the eggshell itself (ES) and the eggshell membrane (ESM). Calcite CaCO3is the main component of the ES, followed by MgCO3 (1%), Ca3(PO4)2 (1%) and 4% of organic matter (Baláz et al., 2016; Tsai et al., 2006).

After many studies to explore some useful applications for the ES, research has shown that they can be used as a livestock feed additive and as fertilizers and they appear to be able to adsorb some organic compounds and heavy metals (Baláz et al., 2016; Velmurugan, 2017; Pettinato et al., 2015; Eletta et al., 2016; Laca et al., 2017; Tsai et al., 2006; Babuponnusami and Hosseini et al., 2017; Köse and Kıvanç, 2011; Elabbas et al., 2016; Pramanpol and Nitayapat, 2006; Hassan and Hassan, 2013; Al-Ghouti and Salih, 2018; Giraldo and Moreno-Piraján, 2014; De Angelis et al., 2017). The naturally porous structure of the eggshell makes it an attractive material option to use as an adsorbent. Each eggshell has been estimated to contain 7000-17000 pores (Laca et al., 2017; Babuponnusami and Velmurugan, 2017; Pettinato et al., 2015; Pramanpol and Nitayapat, 2006).

In this work, removing of BG5 dye using calcined eggshell was investigated for the first-time using batch adsorption system. The purpose of this study is the removal of the BG5 in the aqueous solution with adsorption process at the maximum rate. Therefore, optimum pH and temperature, the optimum amount of adsorbent-adsorbate was investigated to ensure maximum adsorption. Characterization of calcined eggshell was done using Brunauer–Emmett–Teller (BET) and Scanning electron micrographs (SEM) analyzes. Experiments were performed at three different temperatures, 25, 35 and 45°C. UV/VIS Spectrometer (Perkin Elmer Lambda 35) was used for analysis. In the isotherm studies, Baudu and Fritz-Schlunder Isotherm models (Saadi et al., 2015; Ayawei et al., 2017) were applied. The parameters of the two isotherms were determined by non-linear regression analysis.

2. Material and Method

2.1. Materials

Basic Green 5 (BG5; Methylene Green zinc chloride double salt) was obtained from Sigma-Aldrich (CAS no: 224967-52-6) and was used without additional purification steps.Figure 1 shows the chemical structure of the dye. The solution was prepared by dissolving the necessary amount of dye in distilled water.

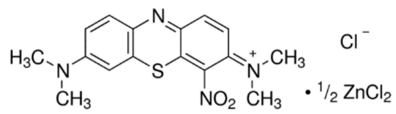

Figure 1. Molecular structure of BG5.

Chicken eggshells used in this study were supplied from bakeries in Istanbul, Turkey. To remove impurity and pollutants, the samples were washed several times with tap water and then with distilled water. The dried eggshells were crushed and screened through a set of sieves to get the geometrical size. 250 mesh and below, were calcined at 800 ºC for 2 h. BET (Brunauer-Emmett-Teller) surface area and SEM (Scanning electron micrographs) analyzes were performed for calcined ESs. According to the elemental analysis run, the components of the eggshell powder are 94% calcium carbonate, 4% magnesium carbonate, 3% protein and 1% of organic matter (Borhade and Kale, 2017).

SEM analysis is often helpful in determining the surface morphology of an adsorbent. SEM image of ES sample after calcination is shown in Figure 2. It was expected that the crystal structure would partially change after heat treatment in calcined ES was determined to be 5.4 m^2g^{-1}.

For pH adjustment purposes, hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) solutions were prepared.

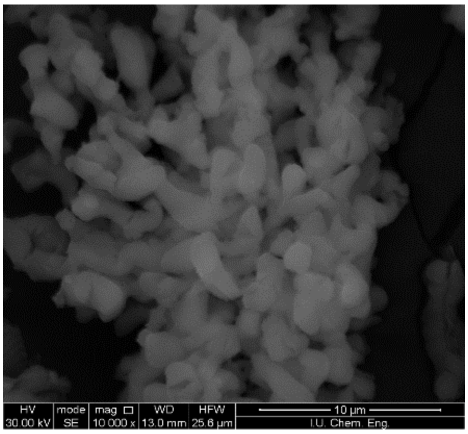

Figure 2. Scanning electron micrographs (SEM) of the calcined eggshell.

2.2. Methods

In this study, batch type process is used for the adsorbtion experiments. In the first stage of the experiments, adsorbent`s period of the equilibrium state was determined. Then, the impact of the amount of the adsorbent was investigated. Following the first stage, in the second stage, impacts of the adsorbent dosage, dye concentrations in the initial stages, and pH were determined. Finally, Baudu and Fritz-Schlunder isotherms which are monolayer and 4-parameters have been applied. The BG5 solution of 20 ppm was prepared by dissolving BG5 dye in deionized water, and dilutions of the stock solution were used in subsequent experiments (10, 15, 20 ppm or $mg.L^{-1}$). In the isotherm experiments, a known amount of adsorbent (0.05-2.0 g) and 5 mL, 15-20 ppm dye solution were mixed in a 50 mL Erlenmeyer flask. The mixture was shaken at a constant speed and temperature in a thermostatic shaker (NUVE BS302 model). Samples were taken out periodically, and the aqueous phase was analyzed by using UV/VIS Spectrometer (Perkin Elmer Lambda 35) at 638 nm against a reagent blank to measure the concentration of BG5. Two parallel experiments under identical conditions were performed for each experiment to have duplication; and their averages were used. The experiments were carried out at 25, 35 or 45 °C.

The amount of BG5 adsorbed on the eggshells surface was calculated using Eq. 1:

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad (1)$$

where qe is the amount of BG5 adsorbed onto adsorbent (mg/g); C_0 and C_e (ppm) are the concentration of BG5 at initial and equilibrium, respectively; V is the volume of solution (L) and m is the mass of the adsorbent (g).

The adsorption efficiency or BG5 removal percentage is calculated using Eq. 2 adopted from Eletta et al. (2016).

$$\textit{Adsorption Efficiency (\%)} = \frac{(C_0 - C_e)}{C_0}.100 \qquad (2)$$

2.3. Adsorption Isotherms

The equilibrium adsorption isotherms are crucial data to understand and interpret the adsorption mechanism. Various adsorbents and some of the most suitable adsorption isotherm models examined in previous studies are summarized in Figure 3 (Saadi et al., 2015). In that work, the two, three and four parameter equilibrium adsorption isotherm models related to monolayer and multilayer adsorption were studied. The parameters of the two isotherms whose results are shared here were determined by non-linear regression analysis. The equations and parameters of Baudu and Fritz-Schlunder isotherms are shown in Table 1 (Saadi et al., 2015; Ayawei et al., 2017).

Table 1. Four-parameter Adsorption Isotherms models used in this study

Isotherm	Formula	Parameters
Baudu	$q_e = \frac{q_B b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}}$	b_0, q_B, x, y
Fritz-Schlunder	$q_e = \frac{C C_e^{\alpha}}{1 + D C_e^{\beta}}$	C, D, α, β

In Table 1, for Baudu isotherm, q_B is Baudu maximum adsorption capacity ($mg.g^{-1}$), b_o is equilibrium constant, x and y are Baudu parameters. For Fritz-Schlunder isotherm, C is Fritz-Schlunder maximum adsorption capacity ($mg.g^{-1}$), D is Fritz-Schlunder equilibrium constant, α and β are Fritz-Schlunder model exponents. The parameters of both isotherms can be determined by nonlinear regression analysis.

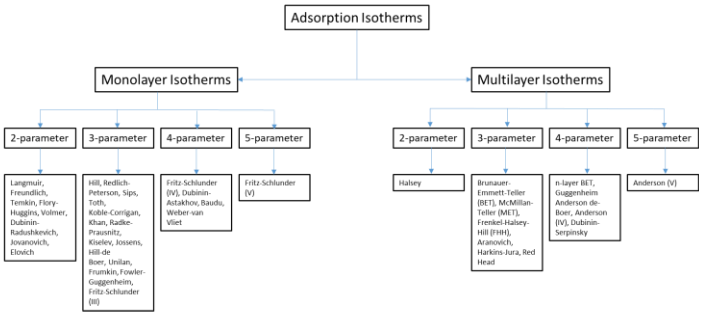

Figure 3. Monolayer and multilayer adsorption isotherm models (Saadi et al., 2015).

2.4. Error Functions

Recently, linear regression analysis is one of the most obvious and feasible tools often applied for the analysis of experimental data obtained from the adsorption process. This was used to confirm the best fitting relationship that measures the distribution of adsorption and the theoretical assumptions of adsorption models and the consistency of adsorption models (Saadi et al., 2015; Ayawei et al., 2017; Ersoy et al., 2014) It is also known that during the transformation into linearized forms of adsorption isotherms, the error formation of the experimental data usually undergoes a change. Non-linear regression analysis is inevitable in this framework because it provides a mathematically rigorous method for determining adsorption parameters using isotherm equations in the original form. Unlike linear regression, nonlinear regression usually involves minimizing the error distribution between the experimental data and the estimated isotherm based on the convergence criteria. If the data obtained from a model is similar to the experimental data, the error value is small; if they differ, it will be a large number. Several methods can be applied to minimize the error values so that the optimum values of the isotherm parameters can be determined. This process is no longer difficult to calculate due to the availability of computer algorithms. RMSE (Root Mean Square Error) method was used in this study. RMSE is defined as Eq. (3) (Saadi et al., 2015; Ayawei et al., 2017):

$$RMSE = \sqrt{\frac{1}{n}\sum_{j=1}^{n}(q_{e,exp} - q_{e,cal})_j^2} \quad (3)$$

where $q_{e,cal}$ is theoretical equilibrium adsorption capacity of adsorbent (mg/g), $q_{e,exp}$ is experimental equilibrium adsorption capacity of adsorbent (mg/g) and n shows the number of adsorption data for a given temperature.

3. Results and Discussion

3.1. Adsorption Experiments

Adsorption equilibrium time was determined 60 min. The effect of amount of adsorbent on the extent of solute adsorption was investigated by varying dose from 0.05 g to 2.0 g adsorbent for each initial concentration of BG5 (10, 15, 20 ppm) at 25ºC. The results obtained with the amount of 0.05 g adsorbent give the highest *q*e value for four different initial concentrations (C_0) (Figure 4). For this reason, 0.05 g of adsorbent has been used for other temperatures (Figure 5).

The dye removal increased with increasing amount of adsorbent. As C_0increases, the amount of q_e and % adsorbed dye increases. The temperature difference did not cause a significant difference on the results. Therefore, the pH effect was only studied at 25 °C. For pH adjustment purposes, hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) solutions were prepared. The value of q_e ranges from 0.82 mg.g^{-1} to 1.87 mg.g^{-1} depending on the C_0 values for different pH values.

The effect of initial solution pH on the adsorption capacity at equilibrium conditions is shown in Figure 6. The results show that increasing the values of pH from 5 to 9 does not affect the dye uptake capacity much.

Piecewise cubic interpolation method is used to fit the adsorption data. Three different plots are obtained using MATLAB®. Figure 4 shows the effect of C_0 and the amount of the eggshell on the adsorption at 25ºC. Figure 5 shows the effect of C_0 and the temperature for 0.05 g adsorbent and Figure 6 shows the effect of C_0 and pH for 0.05 g adsorbent at 25ºC. From the figures, it can be said that the change of temperature, amount of adsorbent and pH values does not cause a significant difference on adsorption.

3.2. Adsorption Isotherms and Error Function

Isotherm parameters and RMSE values are given in Table 2 and 3.

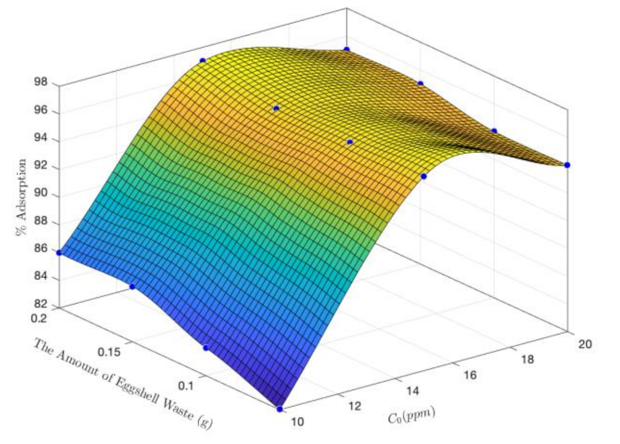

Figure 4. Effect of C_o (initial concentration) and amount of adsorbent on BG5 removal efficiency at 25ºC.

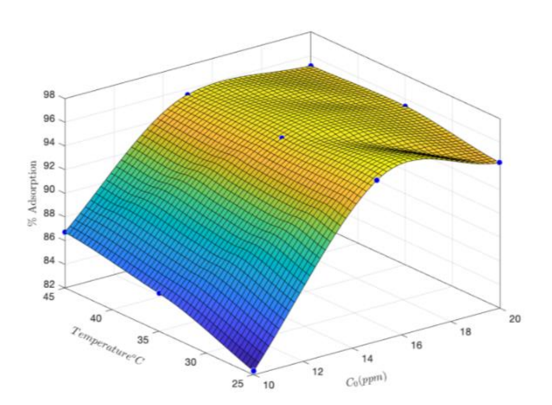

Figure 5. Effect of temperature and C_o on BG5 removal efficiency.

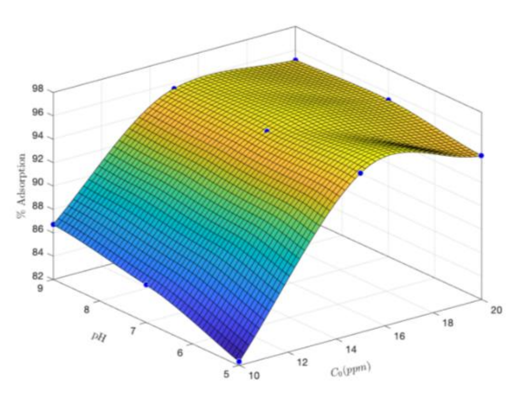

Figure 6. Effect of pH and C_o on BG5 removal efficiency (0.05 g adsorbent, 25 ºC).

Table 2. Baudu isotherm parameters and error functions obtained for adsorption of BG5 onto calcined eggshell for different temperatures.

t, (ºC)	q_B (mg.g^{-1})	b_o	x	y	*RMSE*
25	2.070	9.705	-6.992	0.869	0.002
35	1.927	9.337	6.427	-2.082	0.003
45	1.805	56.412	11.328	-2.525	0.005

Table 3. Fritz-Schlunder isotherm parameters and error functions obtained for adsorption of BG5 onto calcined eggshell for different temperatures.

t, (ºC)	C (mg.g^{-1})	α	D	β	*RMSE*
25	7.9550	-3.7042	3.0748	-5.0374	0.001
35	9.0514	3.9086	4.0854	6.3000	0.003
45	8.7574	4.0672	3.8353	7.3387	0.002

3.3. Comparison with the Literature

Table 4 and 5 compares the results obtained with different adsorbents studied in the literature for BG5 and of different adsorption studies with eggshell waste, respectively.

Table 4. Comparison of BG5 adsorption with different adsorbents.

t, (ºC)	**Adsorbent**	**Isotherm**	**Max. adsorption capacity (mg.g^{-1})**	**Surface area (m^{2}g^{-1})**	**Amount of adsorption (g)**	**Initial concentration of BG5 (ppm)**	**Max. Adsorption (%)**	**Adsorp. time (mins)**	**Ref.**
25	Chicken eggshell waste	Fritz-Schlunder	7.96	5.4	0.05	10	97	60	This study
35		Fritz-Schlunder	9.05						
45		Fritz-Schlunder	8.76						
Room temp.	Ag-NP-AC[a]	Langmiur	167	-	0.01	10-15	>98%	7	Ghaedi et al., 2014
	ZnO-NR-AC[a]	Langmiur	200	-			>96%	6	
25	Activated clay	Langmuir–Freundlich	345	278	1	700	80%	20	Shiau and Pan, 2005
	Montmorillonite	Langmuir–Freundlich	130	165					
	Commercial activated carbon	Langmuir–Freundlich	296	946					
50	Activated carbon from golden shower (*Cassia fistula*)	Langmiur	531	903	0.025	730	78	420	Tran et al., 2017

[a]Ag-NP-AC: silver nanoparticles loaded on activated carbon; ZnO-NR-AC: zinc oxide nanorods loaded on activated carbon

Table 5. Comparison of the capacities of various adsorption processes carried out with eggshell-based adsorbents

Temperature (ºC)	Adsorbate	Isotherm	Maximum adsorption capacity (mg.g^{-1})	References
35	Basic Green 5	Fritz-Schlunder	9	This study
25	Pb^{2+}	Langmiur	34	Kim et al., 2019
	Cd^{2+}		15	
	Cr^{3+}		28	
"laboratory temperature"	Ag^{1+}	Langmiur	56	Baláz et al., 2016
25	Methylene blue	Langmiur	0.8	Tsai et al., 2006
30	Rhodamine B	Langmiur	1.99	Borhade and Kale, 2017
	Eriochrome black T		1.03	
	Murexide		1.57	
25	Ni^{2+}	Langmiur	109	De Angelis et al., 2017
45	boron	Freundlich	2.8	Al-Ghouti and Salih, 2018
25	phosphate	Freundlich	23	Köse and Kıvanç, 2011
20	2,4-Dichlorophenol	Redlich-Peterson	0.34	Baláz et al., 2015
	3,5-Dichlorophenol	Langmiur	0.32	
	Cadmium	Freundlich	32.5	
	Reactive dye	Redlich-Peterson	2.1	

4. Conclusions and Recommendations

In this study, calcined eggshell waste was used as adsorbent for the adsorption of BG5 dye from aqueous stream. Two of non-linear isotherm models (Baudu and Fritz-Schlunder) were applied to the experimental data and isotherm parameters were calculated. The Baudu and Fritz-Schlunder maximum adsorption capacity for all studied temperatures were calculated as about 2 and 9 mg.g^{-1}, respectively. RMSE error values obtained were quite low (between to 0.001 and 0.005). The closer the RMSE value is to zero, the closer the model and experimental results are.

It was also shown that the change of temperature and pH values does not cause a significant difference on adsorption.

The optimum adsorbent (calcined eggshell waste) amount was calculated as 0.05 g for each initial concentration of the dye, and the maximum adsorbed percentage of dye is determined as 97.2062 % at 15ppm (C_o) for 25 ºC. Obtained results indicate that the calcined eggshell can be considered as a good, cheap alternative for adsorption of BG5 dye from aqueous solutions.

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