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Determination of Parameters in Fixed Bed with Industrial Waste Used as Adsorbent

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Abstract

In this study, adsorption studies of aqueous solution of malachite green dye in fixed bed using fly ash were carried out. The effect of adsorbent amount was investigated. Thomas, Adams-Bohart and Yoon-Nelson models were used to evaluate the results obtained. In addition, the correlation between the model and the experimental data was compared using seven non-linear nonlinear functions, while the adsorption dynamics of the fixed bed column were modeled.

Key Words: Adsorption, fixed-bed column, malachite green, fly ash.

1. Introduction

Dyeing processes are an integral part of huge industries including paper, textile, food, cosmetics and paint, resulting in high amounts of water soluble dyes in wastewaters. In the recent years, following increasing industrial and technological progress, dye-wastewater has caused damage to global ecosystems and heavily threatened human health due to its toxicity[1-2]. To date, several approaches have been identified for the removal of dyes including coagulation, solvent extraction, photocatalytic degradation membrane filtration, adsorption, chemical oxidation, and biological oxidation [3]. Comparing to other technology, adsorption method come an economical and feasible method for dye wastewater decontamination due to the cheap adsorbents and efficient treatment effect.

Fixed bed column adsorption has many advantages due to its easy operation and high removal yield. In addition, it can be easily scaled up from a laboratory to an industrial practice. The continuous adsorption process is generally characterized by the socalled breakthrough curves, i.e., a representation of the pollutant effluent concentration versus time profile in a fixed bed column. The design and fixed bed column optimization usually involve mathematical models for the breakthrough curves which are used for both definition and prediction of the experimental data and it is a useful tool for scale-up and design purposes.

Malachite green (MG), a cationic triphenylmethane dye, is widely used in dyeing of silk, cotton, wool, paper, and plastics, as well as in the fish industry as a medical disinfectant to control fungal infections [3].

Fly ash is a byproduct of pulverized coal combustion in electric power generating plants. Fly-ash can find applications in many fields such as the cement industry, brick making, asphalt and concrete plants, waste treatment and soil stabilization, and geopolymers, among others. Fly-ash may be stored at the coal power plants, or they may be deposited in landfills and dumps resulting in extra management costs and negative environmental impact. For this reason, the best solution for the fly-ash is to be reused. However, fly ash recycling is still not much enough and novel applications have to be explored [4].

In this study, the use of fly ash at different amount for removal of malachite green was investigated in the fixed bed. The effect of fly ash amount on adsorption and desorption were investigated.Experimental datas obtained from dye adsorption have been studied by Thomas, Yoon and Nelson, Adam-Bohart models. Eight nonlinear error functions were examined for three models.

2. Materials and Methods

2.1. Materials

Malachite green (MG) was used as adsorbate in this work. Malachite green is cationic dye. MG has the molecular formula $C_{23}H_{25}ClN_2$ and the molecular weight of 364.92 g.mol^{-1}. The spectrophotometric determination of MG was carried out using a Shimadzu UV/Vis spectrophotometer in 601 nm. Measurements in 5 milliliters of cuvettes were used.

Fly ash was transferred to an oven set at 100 °C for 24 h to reduce the water content. The dried sorbent was crushed and milled. The particle sizes were less than 200 mesh. Fly ash, obtained from Elbistan Thermal Power Station, Kahramanmaraş, Turkey.

2.2. Fixed-Bed Column Studies

Continuous fixed bed column studies were performed in a fixed bed column reactor with an inside diameter at 1.5 cm, a column height of 50 cm. In a typical experiment the dye of a known concentration (75 $mg.L^{-1}$) was pumped at a fixed flow rate 4 $ml.min^{-1}$ to the filled with known bed height of adsorbent. The malachite green solutions at the outlet of the column were collected at regular time intervals and the concentration was measured using UV-visible spectophotometer at 601 nm. All experiments were carried out at 25°C. After almost 95-98 % exhaustion the column operation was stopped.

The total adsorbed MG quantity, qtotal ($mg.g^{-1}$) in the column for a given inlet concentration was calculated from Eq.1;

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\, dt \quad (1)$$

where Cad ($mg.L^{-1}$) is the adsorbed MG concentration, Q is the volumetric flow rate (mL min^{-1}) and t_{total} is the total flow time (min).

Equilibrium MG uptake in the column or maximum capacity of the column (qeq) was defined by Eq. (2) as the total amount of MG adsorbed (qtotal) per g of the adsorbent (X) at the end of the total flow time [5].

$$q_{eq} = \frac{q_{total}}{X} \quad (2)$$

2.3.Modelling of Adsorption Column

In order to describe the fixed-bed column behaviour and to scale up it for industrial applications, an accurate model needs to be used. Several simple mathematical models have been developed to describe and possibly predict the dynamic behaviour of the bed in column performance [5]. Therefore, In the present work, adsorption data from fixed bed column studies were analyzed using Adams -Bohart model Thomas model, and Yoon-Nelson model.

Adams-Bohart model assumes that the rate of adsorption is proportional to the residual concentration of the adsorbent and concentration of adsorbing species. This model is used for describing the initial part of the break through curve. Linear form of Adams- Bohart model is given by the following equation:

$$\ln\frac{C}{C_o} = k_{AB}C_o\, t - k_{AB}N_o\frac{Z}{U_o} \quad (3)$$

Where, C_0 is initial dye concentration, ppm; C is concentration of effluent at time t, (ppm); Z is bed depth (cm), N_0 is maximum dye uptake capacity per unit volume of adsorbent column (mg/L); U_0

is linear velocity of influent dye solution (cm/min); K_{AB} is Adams-Bohart rate constant (L/mg.min), The values of K_{AB} and N_0 are determined from the slope and intercept of ln (C_t/C_o) versus t [6].

Thomas model is based on the mass transfer model which assumes that dye migrates from the solution to the film around the particle and diffuses through the liquid film to the surface of adsorbent. This is followed by particle diffusion and adsorption on active site. Linear form of Thomas model for adsorption is:

$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{k_{Th} q_o X}{Q} - \frac{k_{Th} C_o}{Q} V_{eff} \quad (4)$$

Where, C_o is initial dye concentration, ppm; C is effluent dye concentration at time t; ppm KTH is Thomas model constant, L/min.mg; qo is prediction adsorption capacity, mg/gm. x is mass of adsorbent, g; Q is inlet flow concentration, ml/min. The value of K_{TH} and qo are determined from slope and intercept of a plot of ln (C_0/C_t -1) versus t [7].

The main aim of Yoon-Nelson model is to predict the time of column run before regeneration or replacement of column becomes necessary. This model assumes that, the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. Linear form of Yoon-Nelson model is given below:

$$ln \frac{C}{C_o - C} = k_{YN}\, t - \tau\, k_{YN} \quad (5)$$

Where, Co is initial dye concentration, ppm; C is dye concentration at time t, ppm; t is flow time, min.; τ is time required for 50 % breakthrough, min; K_{YN} is Yoon-Nelson rate constant, 1/min. The values of K_{YN} and τ are determined from the slope and intercept of ln (C_t/ (C_0-C_t)) versus t [8].

2.4. Error Functions

In recent years, linear regression has been one of the most viable tools defining the best-fitting relationship quantifying the distribution of adsorbates, mathematically analyzing the adsorption systems. Nonlinear optimization provides method for determining model parameter values but still requires an error function assessment, in order to evaluate the fit of the model to the experimental results [9].

Table 1. List of error functions [9].

Error function	Abbreviation	Definition
Sum squares errors	ERRSQ	$\sum_{i=1}^{p} (q_{exp} - q_{cal})_i^2$
Hybrid fractional error function	HYBRID	$\frac{100}{p-n}\sum_{i=1}^{p}\left[\frac{(q_{exp}-q_{cal})^2}{q_{exp}}\right]_i$
Marquardt's percent standard deviation	MPSD	$100\left[\sqrt{\frac{1}{p-n}\sum_{i=1}^{p}\left(\frac{q_{exp}-q_{cal}}{q_{exp}}\right)_i^2}\right]$
Average relative error	ARE	$\frac{100}{p}\sum_{i=1}^{p}\left(\frac{\lvert q_{exp}-q_{cal}\rvert}{q_{exp}}\right)_i$
Sum of absolute error	EABS	$\sum_{i=1}^{p}\lvert q_{exp}-q_{cal}\rvert_i$
The coefficient of determination	R^2	$\frac{(q_{exp}-\overline{q_{cal}})^2}{\sum (q_{exp}-\overline{q_{cal}})^2+(q_{exp}-q_{cal})^2}$
Nonlinear chi-square test	χ^2	$\sum_{i=1}^{p}\frac{(q_{exp}-q_{cal})^2}{q_{exp}}$
Standard deviation of relative errors	S_{RE}	$\sqrt{\frac{\sum_{i=1}^{p}\left[(q_{exp}-q_{cal})_i-ARE\right]_i^2}{p-1}}$

3. Results and Discussion

3.1. Effect of adsorbent amount on Adsorption

Effect of adsorbent amount was studied by conducting the experiment at 5 g, 7.5 g and 10 g (Fig. 1).

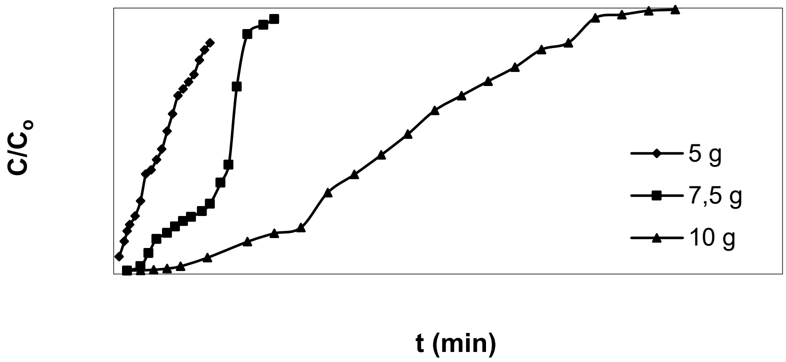

Fig. 1. Effect of adsorbent amount on breakthrough curve

Looking at the table, it was found that as the amount of adsorbent (bed height) increased, MG had more time for contact with fly ash, resulting in a higher dye removal yield of MG. As the amount of adsorbent increases, the slope of the fracture curve decreases, which causes the mass transfer zone to expand.

3.2. Application of the Adams–Bohart Model

The Adams–Bohart model is focused on the investigation of characteristic parameters such as maximum adsorption capacity and kinetic constant. The respective values of No and k_{AB} were calculated from the $\ln C/C_o$ vs. t plots at each adsorbent amount studied, and are presented in Table 2. The breakthrough curves predicted from the Adams–Bohart model were compared with the experimental points, and are shown in Fig. 2.

Table 2. Adams–Bohart model parameters at different adsorbent amount

Adsorbent Amount (g)	K_{AB} (mL/min.mg)	N_o (g/L)	ε (%)
5	0.0635	2091.5	21.967
7.5	0.0685	3704.6	36.52
10	0.0128	2320.5	49.896

3.3. Application of the Thomas Model

The Thomas model was fitted to investigate the breakthrough behavior of MG onto fly ash. The Thomas rate constant (k_{Th}) and the maximum solid phase concentration (q_o) were obtained. Analysis of the regression coefficients indicated that the regressed lines provided a good fit to the experimental data, with R^2 values ranging from 0.971 to 0.977. The values of k_{Th} and qo are presented in Table 3. The bed capacity qo increased with increasing adsorbent amount. Furthermore, the value of qo obtained from the experiment was different from the result calculated for the same conditions. It is clear from Fig. 3.

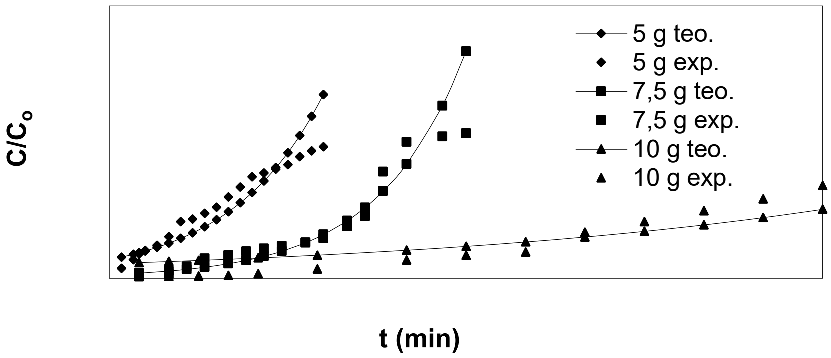

Fig. 2. Adams–Bohart kinetic plot for the adsorption of MG on fly ash: effect of adsorbent amount (MG dye flow rate = 4 mL/min, Dye concentration = 75 mg/L, pH = 4)

Table 3. Thomas model parameters at different adsorbent amount

Adsorbent amount (g)	q_o (mg/g)	K_{Th} (mL/ mg.dak)	ε (%)
5	22.114	0.0296	9.215
7.5	27.44	0.0302	30.25
10	30.79	0.0096	10.214

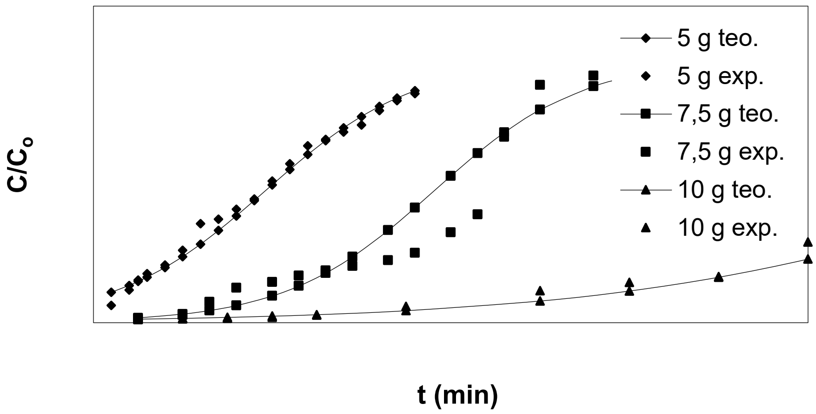

Fig. 3. Thomas kinetic plot for the adsorption of MG on fly ash: effect of adsorbent amount (MG dye flow rate = 4 mL/min, Dye concentration = 75 mg/L, pH = 4)

3.4. Application of the Yoon–Nelson Model

A simple theoretical model developed by Yoon–Nelson was applied to investigate the breakthrough behavior of MG on fly ash. The values of k_{YN} and τ were determined at different adsorbent amount varying between 5 and 10 g. It can be seen from Table 4 that the rate constant k_{YN} decreased with increasing adsorbent amount. Furthermore, the values of τ decreased with increasing adsorbent amount. The theoretical curves are compared with the corresponding experimental data in Fig. 4. It can be seen that the experimental breakthrough curves are very close to those predicted by the Yoon–Nelson model.

Table 4. Yoon–Nelson model parameters at different inlet concentrations

Adsorbent amount (g)	τ (dak)	K_{YN} (1/dak)	ε (%)
5	228.33	0.1186	5.531
7.5	359.81	0.1206	28.982
10	453.16	0.0423	9.668

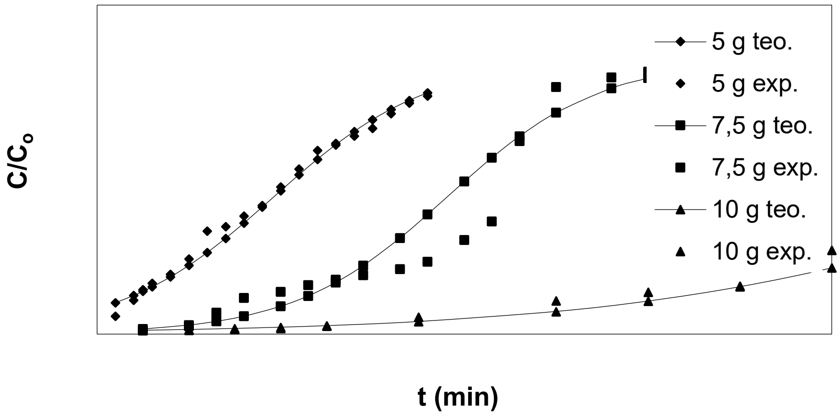

Fig. 4. Yoon–Nelson kinetic plot for the adsorption of MG on fly ash: effect of adsorbent amount (MG dye flow rate = 4 mL/min, Dye concentration = 75 mg/L, pH = 4)

Table.5. Error Function for Models of Fixed Bed Column

	Error analysis (5 g)						
MODEL	R^2	ERRSQ	HYBRID	ARE	EABS	MPSD	X^2
Ad-Boh	0,869	0,274	4,302	3,849	0,134	48,904	0,477
Thomas	0,977	0,015	1,521	1,361	0,127	16,311	0,070
Yo-Nels	0,984	0,013	1,113	1,056	0,089	11,236	0,069
	Error analysis (7.5 g)						
MODEL	R^2	ERRSQ	HYBRID	ARE	EABS	MPSD	X^2
Ad-Boh	0,881	0,394	11,044	9,663	0,357	33,721	0,559
Thomas	0,921	0,164	10,225	8,946	0,435	27,645	0,527
Yo-Nels	0,918	0,139	0,812	6,761	0,182	19,456	0,470
	Error analysis (10 g)						
MODEL	R^2	ERRSQ	HYBRID	ARE	EABS	MPSD	X^2
Ad-Boh	0,867	0,437	13,011	11,566	0,227	27,860	0,713
Thomas	0,983	0,033	0,908	0,807	0,121	9,968	0,078
Yo-Nels	0,953	0,029	0,812	0,765	0,102	8,456	0,070

Conclusions

In the present work, removal of hazardous dye MG in fixed bed column was investigated. Fly ash were used as adsorbent. Fixed bed column studies were conducted in a column of internal diameter 3 cm and length 50 cm. Effect of adsorbent amount on breakthrough curve was studied. It was observed that as the amount of adsorbent (bed height) increased, MG had more time for contact with fly ash, resulting in a higher dye removal yield of MG. Fixed bed column was modeled using Adams-Bohart model, Thomas model and Yoon-Nelson model. The experimental data were in good agreement with theoretical results. The study revealed that fly ash in column can be used as effective adsorbent for removal of azo dyes.

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