Short communication

Effects of process variables on kinetics of methylene blue sorption onto untreated guava (*Psidium guajava*) leaf powder: Statistical analysis

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Abstract

The sorption of methylene blue onto untreated guava leaf powder has been studied. The kinetics of sorption of methylene blue is described by pseudo-second-order model. Effects of initial dye concentration, solution temperature, and adsorbent dosage have been studied. The pseudo-second-order rate constant has been correlated as a function of the system variables. Statistical tools like Student's t-test, F-test, ANOVA and lack of fit have been employed to determine the significance of each coefficient that appeared in the model. Model adequacy has been checked by residual distribution. The proposed model explains 95.1% of the total variation in the response.
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1. Introduction

Dyes are widely used in textile, plastic, leather, and many other industries to color their end products. Considerable amount of these dye are not consumed in the process and appear in the effluent. Many of the dyes are toxic to aquatic life and even affect food chain. Therefore it becomes necessary to treat these effluents for environmental protection [1]. Some of the biological or physico-chemical treatments employed for the treatment of dye effluents include anaerobic/aerobic treatment, coagulation, flocculation, oxidation, membrane separation and sorption [2]. However, adsorption is considered to be superior to other techniques due to its low cost, simplicity of design, high decontamination efficiency and ability to treat dyes in more concentrated forms [3]. Adsorption also eliminates the need for huge sludge-handling processes [4]. Activated carbon as sorbent has been used over decades. High operating cost and problems with regeneration hamper the use of activated carbon for large-scale application [2,3]. This has lead many researchers to search for cheaper substitutes such as coal, fly ash, silica gel, wool wastes, agricultural wastes, wood wastes and many other low-cost materials [3].

Isotherm and kinetics of adsorption of several dyes on different low-cost adsorbents had been extensively studied by several researchers. In order to design appropriate sorption systems it is essential to predict the kinetics of adsorption. Most of the adsorption systems follow pseudo second order kinetics. Many researchers have shown that the second order rate constant varies with process variables like initial dye concentration (C_0), adsorbent dosage (D) and solution temperature (T). But only a few have studied the dependence of rate constant on these process variables. Ho and McKay [5,6] have expressed K_2 in terms of C_0 and D. Vadivelan and Vasanth Kumar [7] have expressed K_2 in terms of C_0. Ho et al. [8] have developed a general empirical relationship between K_2 and the process variables C_0, T, particle size and speed of agitation. The objectives of the present investigation are to establish how the process variables interacted and ultimately affected the rate constant and to develop a semi empirical correlation for the rate constant in terms of the process variables.

The adsorbate methylene blue (MB, chemical formula: $C_{16}H_{18}N_3SCl$; FW: 319.86 g mol^{-1}, λ_{max}: 662 nm, class: thiazine, C.I. classification number: 52015.) was chosen as a model dye because of its well-known adsorption characteristics. The dye is not regarded as acutely toxic, but it can have various harmful effects. Workers handling methylene blue are at risk for photoirritant contact dermatitis (PICD) [9]. High concentration of solid dye in contact with eye has been known to have caused corneal and conjunctival injury in human beings [10].

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Nomenclature

C_0	initial concentration of MB in the solution (mg/dm^3)
C_t	concentration of MB in the solution at time t (mg/dm^3)
D	amount of adsorbent added to the solution (g/dm^3)
K_2	second order rate constant $(g\,mg^{-1}\,min^{-1})$
K_{2mol}	second order rate constant $(g\,mol^{-1}\,min^{-1})$
N	dimensionless number, $1000\,D/C_0$
q_t	dye uptake at time t (mg/g)
t	time (min)
T	temperature (K)
X_i	process variable
X_1	$\ln N$
X_2	reciprocal of absolute temperature (K^{-1})
x_i	dimensionless coded value for X_i
Y	response variable, $\ln K_{2mol}$

Greek symbols

β_0	global mean
β_i	linear effect
β_{ii}	quadratic effect
β_{ij}	interaction effect

Guava or *Psidium guajava* of Myrtaceae family is used as adsorbent. In our earlier report we have shown that guava leaf powder (GLP) possess excellent adsorption capacity for the removal of MB from aqueous solutions [11]. It is a tropical and semitropical plant. It is common in backyards and waste places. The raw leaves contain fixed oil 6%, and volatile oil 0.365%, resin 3.15%, tannin 8.5%, and a number of other fixed substances. Its seeds and leaves possess medicinal value and are traditionally used to treat a number of human ailments [12].

The factorial experimental design involves changing all variables (factors) from one experiment to the next. It determines which factors have important effects on the dependent variable (response) as well as interactions between the factors. Either a linear or a quadratic regression model is used to explain the behavior of the system under study. The significance of each coefficient in the model is determined by Student *t*-test and *p*-values. The variability in dependent variables is explained by the multiple regression coefficient of determination, R^2. Adequacy of the model is tested by analysis of variance (ANOVA) and lack of fit [13–15].

2. Experimental

2.1. Materials

Mature guava leaves were washed thoroughly with distilled water to remove dust and other impurities and dried at 343 K in hot air oven overnight. Dried leaves were then ground, screened to desired size, washed and dried again. Dried GLP was stored in plastic containers for further use. BSS#—100+150 size par-

ticles were used in the present study. The Laboratory grade MB dye was obtained from Himedia India Limited, and used without further purification. A stock solution was prepared by dissolving required amount of dye in double distilled water which was later diluted to required concentrations. All the solutions were prepared in double distilled water. Solution pH was not adjusted as natural pH was favorable for the chosen system [11]. Concentrations of the dye solutions were determined by measuring the absorbance of the solution at the characteristic wavelength ($\lambda_{max} = 662\,nm$) of MB using a double beam UV–vis. spectrophotometer (Systronics 2201). Samples were diluted if the absorbance exceeds 0.8. Final concentration was then determined from the calibration curve.

Dye uptake was calculated using the following formula

$$q_t = \frac{(C_0 - C_t)}{D} X100 \tag{1}$$

2.2. Kinetics

Required amount of guava leaf powder was added to 100 ml dye solution of required concentration taken in 250 ml conical flask. Flasks were then kept in an incubated shaker and agitated at 200 rpm. Samples taken at regular time intervals were filtered and concentration of dye in the filtrates were determined using UV–vis. spectrophotometer.

The kinetic rate data were analyzed using Ho's second order expression [4,5,16]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Plot of t/q_t vs. t is straight line. From the slope and intercept of the plot rate constant and maximum dye uptake can be determined. Batch experiments were conducted by varying concentration (100, 200 and 300 mg/dm^3), dosage (1, 2 and 3 g/dm^3) and temperature (293, 308 and 323 K) one at a time. Thus a total of 27 experiments were conducted. The rate constant for each run was determined using Ho's second order rate expression (Eq. (2)).

3. Results and discussion

Experimental results are given in Table 1. Results were analyzed using Minitab 14. For the analysis of data, dimensionless number N was defined as D/C_0 and $\ln N$ was used as a factor (X_1) in the model. In analogous with Arhenius theory reciprocal of the temperature was used as another factor (X_2) in the model. Also, for statistical calculations, the variables X_i were coded as x_i according to the following relationship.

$$x_i = \frac{(X_i - X_0)}{\Delta X} \tag{3}$$

Codified mathematical model employed for the custom design was

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{4}$$