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Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull

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ABSTRACT

Adsorption of Reactive Black 5 (RB5) in aqueous solution by peanut hull was studied by using Placket–Burman (PB) and Central Composite Design (CCD). Four out of the 7 factors (initial dye concentration, initial solution pH, amount of adsorbent, temperature, particle size, shaking speed and contact time) studied by PB design influenced the adsorption of dye. A CCD was used to develop mathematical model equation. Analysis of variance (ANOVA) showed a high coefficient of determination value ($R^2 = 0.95$). Linear and quadratic effects of the initial dye concentration and linear effect of peanut hull quantity were demonstrated to be very significant ($P < 0.05$) for RB5 adsorption. The interaction between peanut hull dose and initial dye concentration showed remarkable effect on adsorption process. The equilibrium adsorption data of RB5 on peanut hull were analyzed by Langmuir and Freundlich models. The monolayer adsorption capacity (q_m) increased from 50 to 55.55 mg/g with the increase in temperature from 20 °C to 60 °C. The kinetic data were analyzed using the pseudo-first-order and pseudo-second-order adsorption kinetic models. According to these models, the rate constants were calculated for different initial dye concentrations. It can be concluded that the experimental data are well defined with pseudo-second-order kinetic model.

1. Introduction

Dyes usually have a synthetic origin and complex aromatic structures. These colored compounds are widely used in the textile, food, cosmetics, pharmaceutical, tanneries, electroplating factories and host other industries [1]. Dyes (over 7×10^5 metric tons of synthetic dyes) are produced worldwide every year for dyeing and printing purposes and about 5–10% of this quantity is discharged with wastewater. The amount of dye loss depends on the class of dye applied; it varies from 2% loss while using basic dyes to about 50% loss in certain reactive sulfonated dyes [2]. Reactive dyes are representing 20–30% of the total dye market and the most widely used dyes in the textile industry [3]. Many reactive dyes which are typically consisting of azo-based chromophores combined with different types of reactive groups are toxic to some organisms and may cause direct destruction of creatures in water [4]. The discharge of such effluents to the environment is worrying. It can cause some aesthetic problems and also reflection of sunlight penetrated into the water body. This situation interferes the growth of bacteria to a certain level. Thus, some biological degradation processes in natural waters can be damaged to cause on ecological imbalance. Because of their complex structures and high solubility in water, the treatment of these pollutants particularly reactive dyes, in wastewater is troublesome [5]. Sorption has been found an efficient process to remove RB5 from aqueous solutions by various researchers. Activated carbon [6,7], fly ash [6], *Corynebacterium glutamicum* [8], cotton stalk and its hull [9] bone char, peat [7] have been studied as a sorbent for RB5 removal from aqueous solution.

The methods of color removal from industrial effluents include biological treatment, chemical coagulation followed by sedimentation, flotation, adsorption, oxidation and photo catalytic discoloration [10–13]. Among these methods, sorption processes appear to be preferable techniques. Adsorption has been proven to be an excellent method for removing dyes from aqueous solutions because of its significant advantages. It is cheap, easily available, most profitable, easy to be used and most efficient in economical and environmental points of view compared to the conventional treatment.

Activated carbon is perhaps the most widely used adsorbent for the removal of many contaminants but it is prohibitively expensive. Therefore, it is needed to investigate for cheaper substitutes like the solid wastes generated from the agricultural industry [14]. The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is also named biosorption [15]. Bio-adsorbents originated agriculture wastes are cheaper than the already available commercial activated carbon products. So, they can be used economically on a large scale. Recently, a number of studies have focused on the use of different potential agricul-

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Table 1
Factors and levels used in the PBD.

Levels	A Peanut hull dose (g/L)	B Initial pH	C Temperature (°C)	D Dye conc. (ppm)	E Part. Size (Mesh)	F Shaking speed (rpm)	G Contact time (min)
−1	0.75	1	20	50	−30	100	10
+1	1.25	3	40	150	−100	200	420

tural materials as inexpensive bio-adsorbents for the removal of dyes from aqueous solutions. Previously several researchers had proved to use of peanut hull as a biosorbent for removing pollutants such as Cu(II) [14,16], neutral red [17], amaranth, sunset yellow, fast green FCF [13]. Agricultural biomasses mainly consist of lignin, hemi-cellulose and some proteins which make them an effective adsorbent for contaminants [18]. As a bio-adsorbent, the peanut hull is a complex material consisted of mineral, lipid, and cellulose and polyphenol such as catechol, pyrogallic acid and m-trihydroxybenzene, etc. Chemical sorption can occur by the polar functional groups of these constitutes, which include carboxyl groups and phenolic hydroxyl as chemical bounding agents [14]. The peanut hull which can be evaluated as a sorbent since it can also bring unlimited number of economical and environmental benefits to industrial wastewater treatment [17].

Optimization of parameters by the classical method involves changing one independent variable and keeping the other factors constant in the same time. This method investigating effect of one variable at a time may be effective in some cases, but it consumes extra time and material. It requires large number of experimental trials to find out the effects. Also, this method is unreliable and fails to consider the combined effects of all the factors involved. These limitations of the conventional method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design [19]. Response surface methodology (RSM), first described by Box and Wilson, is an experimental approach to identify the optimum conditions for a multivariable system [20]. Recently many statistical experimental design methods have been employed in experimental study's optimization. RSM has been used to make experimental design in some adsorption studies such as methylene blue, acid orange 52 and disperse orange 30 by using activated carbon [21–23].

In this study, adsorption of a reactive dye, RB5 was selected as a model dye material due to its extensive use in textile industry, on peanut hull was investigated by using experimental design procedure such as PB and CCD. So, adsorption process was described mathematically by using RSM. Thermodynamic and kinetic parameters for adsorption process were also analyzed.

2. Materials and Methods

2.1. Experimental design

Response surface methodology may be summarized as a collection of statistical tools and techniques for constructing and exploring an approximate functional relationship between a response variable and a set of design variables [24]. The most extensive application of RSM can be found in the chemical and biological processes, in various situations where several input variables influence some performance measures, called the response, in a way that is difficult or impossible to describe with a rigorous mathematical formulation. In these cases, it might be possible to derive an expression for the performance measure based on the response values obtained from experiments at some particular combination of the input variables. The variable levels X_i were coded as x_i according to the following equation such that X_o corresponded to the central value:

$$x_i = \frac{X_i - X_o}{\Delta X_i}, \quad i = 1, 2, 3, ..., k \tag{1}$$

where; x_i is the dimensionless value of an independent variable; X_i is the real value of an independent variable; X_o is the real value of an independent variable at the center point. ΔX_i is the step change. Codification of the levels of the variable consists of transforming each studied real value into coordinates inside a scale with dimensionless values, which must be proportional at its localization in the experimental space [25].

The behavior of the system are explained by the following quadratic equation:

$$y = \beta_o + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{2}$$

where, β_o is the constant, β_i the slope or linear effect of input factor, β_{ii} the quadratic effect on input factor, β_{ij} is the linear interaction effect between input factors [26].

2.1.1. Placket–Burman design

The effect of seven factors such as: initial dye concentration, initial solution pH, amount of adsorbent, temperature, particle size, shaking speed and contact time were selected as independent factors and the adsorption yield was chosen to be response to the process. The parameters were varied; two levels and the minimum and maximum ranges were selected for parameters are given in Table 1. PB design requires 12 runs that were employed with a replicate and thus a total of 24 experiments were done for adsorption of RB5.

2.1.2. Central composite design

Based on the results of PB and the effect of four parameters, such as initial dye concentration, initial solution pH, amount of adsorbent and contacting time, the adsorption of RB5 using CCD was studied. Other parameters for adsorption process were constant at of temperature 25 °C; particle size of 50 mesh, shaking speed of 150 rpm. Each factor in the design was studied at five different levels as shown in Table 2. Experiments were planned to obtain a quadratic model consisting of 2^4 trials plus a star configuration and six centre points. Thirty experiments were conducted in duplicate.

The results of the CCD were then used to fit quadratic equation by multiple regression procedure. This gives an empirical model that related to the response of measured independent variables of the experiment. Data obtained from the experimental runs were

Table 2
Experimental range and levels of the independent variables for CCD.

Code	Variables	−α	−1	0	+1	+α
x_1	Peanut hull dose (g/L)	0.5	0.75	1.0	1.25	1.5
x_2	Initial pH	0.5	1	1.5	2	2.5
x_3	Dye concentration (ppm)	50	100	150	200	250
x_4	Contact time (min)	30	120	210	300	390