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Isotherm modeling, kinetic study and optimization of batch parameters for effective removal of Acid Blue 45 using tannery waste

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ABSTRACT

The present study describes the potential of Chrome Shavings (CS), a tannery waste, for the removal of AB 45 dye. A Central Composite Design was employed for framing the experimental design matrix. To facilitate the optimization of various batch parameters (pH, adsorbent dosage and initial dye concentration), Response Surface Methodology (RSM) was applied. The numerical optimization was performed in two different ways by setting the lower and upper limits within the range of $-\alpha$ and $+\alpha$. From an industrial perspective the second numerical optimization was considered to be best, which predicted 92.93% as highest removal efficiency when adsorbent dosage, pH and initial dye concentration were found to be 2.64 g/L, 0.98 and 234.09 mg/L respectively. This result was validated by performing a confirmatory test which showed a 1% deviation from the predicted model. The constants of different isotherms, kinetics and thermodynamics were studied. The maximum adsorption capacity of CS obtained from Langmuir isotherm was found to be 83.33 (303 K), 90.90 (313 K) and 100 mg/g (323 K). The activation energy was calculated as 845.15 (303 K), 912.87 (313 K) and 1118.034 kJ/mol (323 K) using D–R isotherm. The kinetics of adsorption followed pseudo-second-order reaction and the values of rate constant were calculated as 0.0013(303 K), 0.0016(313 K) and 0.0021 mg/g/min (323 K). The result of Weber–Morris model revealed that this adsorption process involved complex rate controlling steps. From the Boyd's model, the major rate controlling step was observed to be film diffusion. The thermodynamics study revealed that the adsorption process was spontaneous and endothermic in nature. The thermodynamics parameters such as Gibb's free energy ($\Delta G°$), change in enthalpy ($\Delta H°$) and change in entropy ($\Delta S°$) at normal temperature were found to be -6.31 kJ/mol, 11.98 kJ/mol and 0.06 kJ/mol/K respectively. The basic surface structural changes before and after adsorption were studied using SEM and FT-IR analysis. Infrared studies indicated the influence of amino, hydroxyl and carboxyl groups in the adsorption of AB 45 dye. This study depicted that CS can be used as an effective and economically viable adsorbent for the removal of AB 45 dye.

1. Introduction

In recent years, contamination due to various industrial activities has become a serious threat to the environment. Rapid industrialization and urbanization lead to water scarcity and environmental pollution [1]. In industries like textiles, food, cosmetics, paper and plastic, dyes are used for coloring purposes. Textile is one of the main industries which utilize dyes, chemicals and water during the process of fabric manufacture. These industries produce a large amount of colored wastewater, which has a strong persistent color and a high BOD loading making it esthetically and environmentally objectionable [2]. Some of these dyes are toxic and are suspected to have carcinogenic and mutagenic effects [3]. Dyes can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [4]. During the process of decomposition, many dyes release chemicals as byproducts, which reduce the sunlight penetration and photosynthetic activities [5]. AB 45, being an organic dye, is commonly used for dyeing cotton, wool and silk. The use of this dye has several harmful effects on human beings and affects the eye, skin as well as cause respiratory problems and digestive tract irritation. The excessive release of hazardous organic and inorganic pollutants due to the industrial activities initiated the research work towards its detection and removal [6–9]. There are several methods in the treatment of colored wastewater such as coagulation, flocculation, reverse osmosis, precipitation, oxidation, reduction, membrane filtration, ultrasonic treatment, aerobic and anaerobic treatment, biochemical degradation and adsorption, ion exchange, photo-oxidation process, electrochemical, microbiological decomposition and ozonation [10–22]. Among the above specified methods, adsorption is considered as the most efficient method for the removal of pollutants from industrial effluents [23]. It has been widely used for the removal of metals [24–27], dyes [28–36] and pesticides and for storage and oil spillage control in various fields [37]. The commonly used adsorbents are activated carbon, alumina, silica and

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Nomenclature

C_e	Equilibrium concentration (mg/L).
q_e	Amount of ion adsorbed at equilibrium time (mg/g).
q_{max}	Maximum quantity of metal ions adsorbed on the monolayer surface (mg/g).
K_L	Langmuir Constant (L/mg).
C_o	Initial dye concentration (mg/L).
R_L	Dimension separation factor.
K_f	Freundlich constant.
1/n	Freundlich exponent.
A_T	Temkin constant related to heat of sorption (J/mol).
K_T	Temkin isotherm constant (L/mg).
β	Dubinin–Radushkevich isotherm constant related to adsorption capacity (mol^2/J^2).
ε	Polanyi potential (J/mol).
R	Universal gas constant (8.314 J/(mol K)).
T	Temperature (K).
q_t	Adsorption capacity of CS at equilibrium at time t (mg/g).
K_1	Pseudo-first order rate constant (min^{-1}).
K_2	Pseudo-second-order-rate constant (mg/g/min).
K	Adjustment parameter in Power function (mg/g/min).
α	Initial adsorption rate constant (mg/g/min).
β	Extent of surface coverage and activation energy for chemisorption (g/mg).
K_p	Intra-particle diffusion constant ($mg/g/min^{0.5}$).
C_i	Intercept of intra-particle diffusion equation.
f	Fractional attainment of equilibrium at different times t.
B_t	Function of f.
ΔG°	Gibb's free energy (kJ/mol).
ΔH°	Change in enthalpy (kJ/mol).
ΔS°	Change in entropy (kJ/mol/K).

ferric oxide. In spite of its high adsorption capacity, the cost of these adsorbents is prohibitive. Hence many researchers have started investigating the adsorption of dyes on various industrial wastes [38–40] such as bagasse fly ash [41], coal fly ash[42], sludge from the electrocoagulation process [43], solid waste from leather industries [44], blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry [45], solid waste of soda ash plant [46], steel and fertilizer industry waste [47], and metal loaded skin split waste [48]. The use of leather waste i.e. CS represents an alternative adsorbent for the treatment of colored wastewater. It was found that CS has a high sorption capacity of organic dyes [49]. The removal of dye is influenced by various factors, and it is observed that the interaction of those factors plays a vital role. The conventional approach requires a large number of experiments which makes it time-consuming. Further it does not depict the effects of combinations of all factors involved. These limitations can be eliminated by using statistically designed models like Response Surface Methodology (RSM). RSM is an empirical model which is used to appraise the relationship between independent factors and the response. The main objective of the RSM is to optimize the process and to evaluate the significance of various factors even in the occurrence of multiple interactions [50].

This study focuses on the removal of AB 45 dye using chrome shavings as an adsorbent. The main objectives of this study are:

i) to evaluate the suitability of linear, two-factor interaction (2FI), quadratic and cubic models.
ii) to examine the combined effect of various influencing factors
iii) to investigate the suitability of different isotherms and kinetic models
iv) to identify the sorption mechanism of AB 45 on chrome shavings and
v) to numerically optimize these variables for the removal of AB 45 dye.

2. Materials and method

2.1. Characteristics of chrome shavings and Acid Blue 45

The adsorbent material was supplied from a local leather industry in Vellore. The material was dried at room temperature for five days before its usage. Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers. The physico-chemical characteristics of AB 45 and chrome shavings are given in Table 1.

2.2. Experimental design

The most popular RSM design is the Central Composite Design (CCD). The CCD was used to develop a correlation between the variables and the adsorption of AB 45 on CS. The number of experiments (N) can be estimated using the following Eq. (1):

$$N = 2^n + 2n + n_c \tag{1}$$

where, n is the number of factors and n_c is the number of central points. The independent variables chosen for this study were i) A — Adsorbent dosage, ii) B — pH and iii) C — Initial dye concentration. A 2^3 CCD which consists of 8 factorial points, 6 axial points and 6 replicates resulted in 20 different combinations of experiments. Experimental runs between 15 and 20 at the center point were used to determine the error of experiments and reproducibility of the data. The coded values of the different process variables were found from Eq. (2):

$$x_i = (X_i – X_0)/\Delta X, i = 1, 2, 3..., k \tag{2}$$

where, x_i is the dimensionless value of a process variable, X_i is the real value of an independent variable, X_0 is the value of X_i at the center point and ΔX is the step change. The low and high values of independent variables are coded as −1 and +1 respectively and augmented by 2n axial points [(±α, 0, 0), (0, ±α, 0) and (0, 0, ±α)] and n_c center points. The range and the levels of independent variables are given in Table 2. Using a second order polynomial equation, a quadratic model was employed, which correlates between the three independent variables and response (AB 45 removal, %) which is given by Eq. (3):

$$Y_1 = \propto_0 + \sum_{i=1}^{k} \propto_i X_i + \sum_{i=1}^{k} \propto_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i<j=2}^{k} \propto_{ij} X_i X_j + \in \tag{3}$$

where, Y_1 is the removal efficiency (%), α_0 is the offset term, α_i is the first order main effect, α_{ii} is the second order main effect, α_{ij} is the interaction effect, X_i is the linear term, X_i^2 is the quadratic term and

Table 1
Characteristics of chrome shavings and Acid Blue 45.

Characteristics of chrome shavings	
Average moisture (%)	25.42
Ash (%)[a]	11.29
Chromium oxide (%)[a]	5.42
Fat (%)[a]	3.21
Specific area (m^2/g)	1.23
Characteristics of Acid Blue 45	
Appearance	Blue
Molecular formula	$C_{14}H_8N_2Na_2O_{10}S_2$
Molecular weight	474.33 g
λ_{max}	598

[a] Based on dry weight.