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Research article

Combined Homogeneous Surface Diffusion Model – Design of experiments approach to optimize dye adsorption considering both equilibrium and kinetic aspects

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A B S T R A C T

Adsorption, a popular technique for removing azo dyes from aqueous streams, is influenced by several factors such as pH, initial dye concentration, temperature and adsorbent dosage. Any strategy that seeks to identify optimal conditions involving these factors, should take into account both kinetic and equilibrium aspects since they influence rate and extent of removal by adsorption. Hence rigorous kinetics and accurate equilibrium models are required. In this work, the experimental investigations pertaining to adsorption of acid orange 10 dye (AO10) on activated carbon were carried out using Central Composite Design (CCD) strategy. The significant factors that affected adsorption were identified to be solution temperature, solution pH, adsorbent dosage and initial solution concentration. Thermodynamic analysis showed the endothermic nature of the dye adsorption process. The kinetics of adsorption has been rigorously modeled using the Homogeneous Surface Diffusion Model (HSDM) after incorporating the non-linear Freundlich adsorption isotherm. Optimization was performed for kinetic parameters (color removal time and surface diffusion coefficient) as well as the equilibrium affected response viz. percentage removal. Finally, the optimum conditions predicted were experimentally validated.

1. Introduction

Dyes are used in textile, ink, paints, and food industries among many others (Porhemmat et al., 2017). However, these industries are also responsible for polluting water bodies and underground water through the discharge of their effluents containing predominantly dyes (Geetha et al., 2008). These dyes may be hazardous and carcinogenic (Konicki et al., 2017) and may also impart an unpleasant color and odor to the effluents. The dyes may affect marine ecosystem by inhibiting the transmittance of sunlight through water (Kulkarni et al., 2017). Azo dyes containing one or more azo groups belong to the largest class of dyes used in textile, food, pharmaceutical and paper industries. These are very stable to ultraviolet and visible light irradiation and also resist aerobic degradation. Most of these azo dyes are resistant to biological and chemical degradation (Sun et al., 2009) because of which they persist in the environment. Most azo dyes are carcinogenic and mutagenic (Konicki et al., 2017). Arulkumar et al., 2011 point out to the prevalence of considerable azo dye pollution from textile industrial effluents in the several parts of Tamil Nadu, India. They have also expressed that relatively lesser amount of work has been carried out involving the Orange G azo dye.

Adsorption of solute components on activated carbon has been one of the most preferred methods for removing pollutants from wastewater. Activated carbon is versatile owing to its large surface area, high adsorption capacity, variable surface chemical composition and ability to adsorb different types of pollutants (Mezohegyi et al., 2012). There is also the possibility for recycling and reusing the adsorbent and it does not form sludge. However, the adsorption process itself may depend in a complex fashion upon a number of process variables such as temperature, pH, initial solution concentration, adsorbent loading, mechanical agitation rate, etc. Hence, an efficient experimental strategy is required to identify the significant factors and their interactions that influence dye removal. The statistically based Design Of Experiments (DOE) approach helps in economic and efficient experimentation. It enables handling of a large number of experimental variables, also called as factors. The DOE approach not only identifies significant individual factors but can detect interactions among them as well.

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Several researchers have adopted DOE to identify the main factors and their interactions that influence the adsorption process (Arulkumar et al., 2011; Asfaram et al., 2016; Auta and Hameed, 2011a; Chaudhary and Balomajumder, 2014; Pavlovic et al., 2014).

From an industrial perspective, optimum set of operating conditions of a batch adsorption process that lead to both rapid as well as considerable removal of the harmful compounds from aqueous solutions need to be identified. This involves consideration of both kinetic and thermodynamic aspects of the adsorption process. Adsorption kinetics is important to determine important design parameters such as adsorption tank dimensions and residence time (Walker, 1999). Faster kinetics results in lower batch processing time. A rigorous mathematical model is essential to obtain relevant parameters from the generated experimental kinetics data. These parameters may be used to optimize the process. Empirical kinetic models (pseudo-first order and pseudo-second order) have been used in literature in preference to rigorous first-principles models owing to the latter's complexity and simulation effort (Garcia-Reyes and Rangel-Mendez, 2010). However, these empirical kinetic models assume that adsorption is a pseudo chemical reaction (Dotto and Pinto, 2011; Raji and Pakizeh, 2014) and may not inherently capture all the underlying mass transport phenomena involved in adsorption. For rigorous simulation of dye adsorption kinetics, Homogeneous Surface Diffusion Model (HSDM) has often been effectively used (Capelo-Neto and Silva Buarque, 2016; Dotto and Pinto, 2011; Jia et al., 2009; Kim et al., 2016). The HSDM considers the external convective transport (or film) resistance around the particle surface and the intra particle diffusion through the adsorbent that is assumed to be a homogeneous medium. Literature tends to suggest that the HSDM is pertinent when the intra particle diffusional resistance is more important than the film resistance (Capelo-Neto and Silva Buarque, 2016; Kim et al., 2016).

A suitable experimental design such as Central Composite Design (CCD) or Box Behnken Design (BBD) has been used in literature to correlate responses i.e. experimental outputs with the significant experimental factors. For the experimental response chosen, a correlation involving the significant factors was developed. The correlation has been subsequently used in a few studies for optimizing the associated experimental response. In these exercises, the researchers have not usually incorporated the adsorption kinetics effects to ensure that the chosen conditions for maximizing pollutant removal also ensured its rapid removal. In this study, we demonstrate how DOE and detailed kinetic modeling involving HSDM may be combined to identify optimal conditions that enable rapid and considerable removal of the pollutant by the adsorption process. To our knowledge, the following objectives that are explored in this work are novel.

a. Using the kinetic parameter i.e. the homogeneous surface diffusion coefficient as response in subsequent optimization. The surface diffusion coefficient parameter for each experimental condition is estimated by fitting the HSDM simulation predictions with batch adsorption kinetics experimental data
b. Identifying optimal operating conditions that simultaneously maximize adsorption i.e. extent of dye removal and ensure fast kinetics

Further insight into the adsorption process is attempted through carbon surface characterization, thermodynamic and kinetic analysis. Optimization is carried out to identify conditions that individually maximize the adsorption extent and adsorption rate. This is followed by simultaneous optimization of both adsorption extent and rate. The different optimal conditions identified are then compared and suitable conclusions are drawn.

2. Materials and methods

2.1. Adsorptive

An anionic monoazo dye, namely Acid Orange 10 was chosen as the representative pollutant since it belongs to one of the most commonly used azo dyes. The properties of AO10 dye are shown in supplementary materials (Table ST1). It is an anionic dye and is distributed as a disodium salt.

2.2. Adsorbent

Among different commercial options, coconut shell charcoal based steam activated carbon (SAC) procured from Active Char Products Pvt. Ltd. Edyar, Kerala, was chosen owing to its high porosity and eco-friendly production procedure. The average particle size selected for conducting the experiments was 0.463 mm. After sieve analysis, the carbon was washed several times thoroughly with deionized water. Nearly complete removal of any fines present was ensured by allowing the activated carbon to settle for a couple of hours. The SAC was then dried in a hot air oven at 120 °C for a period of 24 h to remove moisture. The dried SAC was then stored in a desiccator in order to avoid contact with moisture present in the air.

2.3. Batch adsorption vessel

Adsorption kinetic experiments were carried out in a water jacketed batch adsorption vessel. Water from a constant temperature bath (procured from R.K. Scientific Pvt. Ltd., Chennai, India) was circulated inside the jacket for controlling the process temperature at the desired values. The vessel was designed following standard specifications (McCabe et al., 1993). Baffles were placed vertically along the circumference of the inner wall of the vessel to prevent vortex formation at higher rpms. The vessel was fitted with a mechanical stirrer (also procured from R.K. Scientific Pvt. Ltd.). A digital controller maintained the stirrer speed at 400 rpm.

2.4. Statistical design of experiments

The Central Composite Design experimental design strategy is implemented in this work. This is a popular second order design and considers main factors, binary interactions between factors and quadratic terms of factors (Dil et al., 2016). Design-Expert® version 10.0.0 (Stat-Ease Inc., Minneapolis, MN, USA) was used to generate the experimental design and to analyze the responses. pH, temperature, adsorbent dosage and initial dye concentration were chosen as the process variables. The axial point was located at a distance of $\sqrt{2}$ from the geometric center of the design in this CCD.

The experimental runs were performed in a randomized fashion in order to minimize systematic error. Each parameter was varied at three different levels viz. at a low level, a high level and the center point. In the coded form, a low level is indicated by -1, a high level is indicated by $+1$ and a center point is indicated by 0.

Table 1 shows the factors and the actual numerical values of their levels that were assigned in the experimental design. The ranges of values for the factors, as shown in Table 1, have been chosen after performing considerable number of preliminary i.e. screening experiments. The CCD also incorporated axial points which further served to expand the basic 2^3 factorial design. The temperature range was set from 25 °C to 45 °C in the factorial design. However, when the axial points were also considered, the range expanded from 20.9 °C to 49.1 °C. The concentration ranges were chosen after deciding upon the adsorbent dosages. During the course of preliminary experiments, very high feed concentrations