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Removal of tartrazine by activated carbon biosorbents of *Lantana camara*: Kinetics, equilibrium modeling and spectroscopic analysis

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ABSTRACT

Preparation of the activated carbon biosorbents from *Lantana camara* weed by sulphuric acid activation was carried out. Laboratory prepared activated carbon was used as adsorbents for the removal of an acidic dye tartrazine from aqueous solutions. Liquid-phase adsorption experiments were conducted and the maximum adsorption capacity of activated carbon was determined. The effects of various process parameters, i.e., temperature, pH, initial tartrazine concentration, contact time on the adsorption capacity of activated carbon were investigated. The kinetic models for tartrazine adsorption onto activated carbon were studied. Freundlich isotherm (K_F, 98.401 L g^{-1}) showed better fit than Langmuir isotherm (Q_0, 90.900 mg g^{-1}) for the activated carbon. The rates of adsorption were found to confirm the pseudo-second-order kinetics with good correlation. The separation factor (R_L) revealed the favorable nature of the isotherm of the tartrazine-activated carbon system. The values of activation parameters such as free energy (ΔG°, −10.346 to −10.983 kJ mol^{-1}), enthalpy (ΔH°, 22.976 kJ mol^{-1}) and entropy (ΔS°, 154. 555 J mol^{-1} k^{-1}) were determined, respectively, indicating that the adsorption was spontaneous, endothermic and favorable process in nature.

Introduction

Discharge of dye bearing effluents into the water bodies has raised much concern because of potential health hazards associated with the toxicity and their byproducts into the food chains of humans and aquatic animals. The synthetic dyes when enters into the water alters the aqueous chemistry by changing the solution pH, color, chemical oxygen demand and causes hindrance in the growth of microbial organisms [1]. Dye also impedes the penetration of solar-light, thus changes the photosynthetic activity. Therefore, there is an urgent need to remove dyes before effluent is discharged into receiving aquatic system. Currently, the most popular treatment methods for dye-laden wastewater are combinations of biological treatment [2], chemical coagulation [3,4], photocatalytic degradation [5], electrochemical degradation [6], photo-Fenton processes [7], and activated carbon adsorption [8–10].

Efforts should be made to minimize the use and generation of hazardous chemicals, while increasing the treatment efficiencies of the wastewater generated. Therefore, investigation of alternative and appropriate technologies for the removal of toxic dyes is of utmost importance. Adsorption onto activated carbon is proven to be very effective in treating dye-laden industrial effluents. However, in view of high cost and associated problems of regeneration, there is a constant search for alternative low cost adsorbents. Such types of adsorbents includes mustard husk [11], chitosan [12,13], cactus [14], oil palm trunk fibers [15], durian (*Durio zibethinus* Murray) peel [16], almond shell [17], sugarcane bagasse [18,19], and sphagnum moss peat [20].

Lantana camara L., (hereafter *Lantana*), a native of tropical America, belongs to the family Verbenaceae and has been described as one of the world's ten worst weeds [21]. *Lantana* is an invasive species and has covered large areas in India, Australia, and much of the Africa. *Lantana* is a significant weed of which there are some 650 species in over 60 countries. The plants can grow individually in clumps or as dense thickets, crowding out more desirable species. In disturbed native forests it can become the dominant understorey species, disrupting succession and decreasing biodiversity. It is also shown that exotic species invasions

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influence distribution and abundance of native species and affect regeneration of native flora. Yet, this potential biomaterial has not been applied for remediation of azo dye-laden wastewaters.

In view to fill in the paucity of published data on the use of biomass based adsorbents for removing tartrazine dye molecule, in the present study, the removal of chemical grade tartrazine was studied by using activated carbon of *Lantana*. Tartrazine was selected as a model dye because it is widely used in pharmaceuticals, food products, drugs, cosmetics and for dying of textile fibers [22]. Tartrazine is considered to be highly toxic for humans as it acts as hyperactivity and causes asthma, migraines, eczema, thyroid cancer and other behavioral problems [23]. Batch adsorption experiments were conducted using synthetic aqueous solutions of tartrazine and the effects of initial dye concentration, initial pH of solution, and temperature were investigated. The kinetics of adsorption has been studied, and various kinetic models, such as pseudo-first-order, pseudo-second-order and intra-particle diffusion models were tested with experimental data for their validity. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm techniques. Experimental data have been fitted to the Langmuir and Freundlich isotherm models to determine the best isotherm to correlate the experimental data. Thermodynamics of the adsorption process has also been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

Materials and methods

Materials

Tartrazine (trisodium (4*E*)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazono]-3-pyrazolecarboxylate; C.I., 19140; molecular formula, $C_{16}H_9N_4Na_3O_9S_2$; molar mass (534.30 g mol^{-1})) was purchased from British Drug House, Poole, England. Fig. 1 shows the chemical structure of the tartrazine molecule. Tartrazine stock solutions (1000 mg L^{-1}) were prepared by dissolving the required amount in double distilled water, and the working solution was prepared daily with the required dilution. The concentration of the dye was determined at 427 nm. Solution pH was measured using a pH/ion meter (pH meter 335, Systronics, Ahmedabad, India) and absorption studies were carried out using UV–vis spectrophotometer (spectrophotometer 2203, Systronics, Ahmedabad, India). All chemicals with the highest purity analytical reagent grade available were purchased: NaOH, HCl and NaCl (E. Merck, Mumbai, India). Sulphuric acid (98 wt%) obtained from Sigma–Aldrich was used as an activating agent.

Preparation of the activated carbon of Lantana

Lantana was collected from the University campus, University of Allahabad, Allahabad, India. The collected material was first washed with distilled water twice and dried in sunlight for 3–5 days. Then, the completely dried material was crushed down to a powder and washed again 5 times with double distilled water and dried in a hot air oven (Gupta scientific industries, Ambala Cant, India) up to 120 °C for 24 h.

The powdered *Lantana* biomass was mixed with concentrated sulfuric acid in 1:1 ratio. This mixture was dried at 110 °C for 24 h to prepare the impregnated sample. The impregnated sample was carbonized at 600 °C under nitrogen (N_2) flow of 30 mL min^{-1} at a heating rate of 5 °C min^{-1}. After carbonization, the sample had been cooled down under N_2 gas flow; the carbonized sample was washed several times with double distilled water to remove residual chemicals. The washing and filtration steps were repeated until the pH of filtrate became neutral. The washed sample was oven dried at 110 °C for 24 h to prepare the activated carbon. The oven dried powder was then sieved with 44 BSS mesh. The fine particles were selected for the adsorption experiments, placed in air-tight glass bottles and finally kept in desiccators.

Characterization of Lantana *adsorbent*

Infrared spectra of unloaded and dye-loaded adsorbents at the optimum pH for maximum dye removal were obtained by the use of a Fourier Transform Infrared Spectroscopy using a (FTLA 2000, ABB, Canada) to determine the surface functional groups. Scanning electron microscopy (SEM) was used to study the surface morphology of the adsorbent. SEM studies were carried out using a scanning electron microscope (Scanning Electron Microscope-Zeiss EVO 40) at an electron acceleration voltage of 20 kV. Prior to scanning, the adsorbent was coated with a thin layer of gold using a sputter coater to make it conductive. X-ray diffraction analysis was performed by Philips PW1050 X-pert diffractometer using Cu-K_α(=0.15406 Å) radiation source in order to determine the degree of crystallinity or amorphous nature of activated carbon. The surface area and pore volume were also determined with a BET (Brunauer, Emmett and Teller) surface area analyzer (Micromeritics ASAP 2020, surface area analyzer), by means of adsorption of ultra pure nitrogen at 77 K. The elemental analysis was performed using Elemental Analyzer (CHN Autoanalyzer, Australia). The pH at pH_{zpc} of the activated carbon of *Lantana* was determined by the solid addition method [24,26]. Initial pH of 0.1 N KNO_3 solutions (pH_i) was adjusted from pH 2–12 by adding either 0.1 N HCl or 0.1 N NaOH. Adsorbent dose (0.5 g) was added to 50 mL of 0.1 N KNO_3 solutions in 150 mL conical flasks and stirred for 30 min of contact time and final pH (pH_f) of solution was

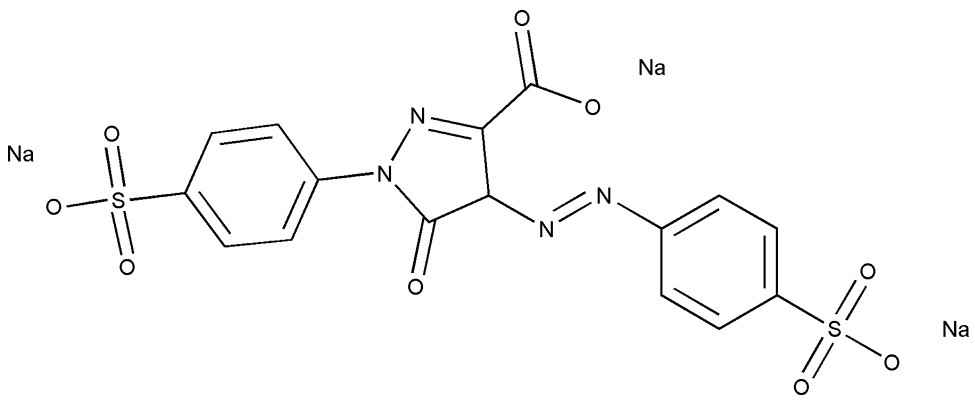

Fig. 1. Chemical structure of tartrazine molecule.