Alexandria Engineering Journal (2016) xxx, xxx–xxx

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Alexandria University

Alexandria Engineering Journal

www.elsevier.com/locate/aej
www.sciencedirect.com

ORIGINAL ARTICLE

Evaluating the potential of a Nigerian soil as an adsorbent for tartrazine dye: Isotherm, kinetic and thermodynamic studies

M.O. Dawodu [a], K.G. Akpomie [b,*]

[a] Department of Chemistry and Industrial Chemistry, Bowen University, Iwo, Osun State, Nigeria
[b] Projects Development Institute (PRODA), Federal Ministry of Science and Technology, Enugu, Nigeria

Received 20 May 2015; revised 4 August 2016; accepted 7 August 2016

KEYWORDS

Tartrazine;
Anionic dye;
Sorption;
Soil

Abstract The release of toxic tartrazine dye from industrial effluent into the environment is of public health concern. This study therefore aimed at the removal of tartrazine from solution using Nigerian soil as a low cost potential sorbent. The sorbent was characterized by the Fourier transform infrared spectrophotometer and Scanning electron microscope. Batch sorption methodology was used to investigate the effect of pH, adsorbent dose, dye concentration, contact time and temperature. The sorbent recorded a Brunauer, Emmett and Teller surface area of 9.8 m^2/g and pH point of zero charge of 5.8. Optimum sorption was achieved at pH 2.0, contact time of 120 min, adsorbent dose of 0.05 g and tartrazine concentration of 50 mg/L. Equilibrium isotherms were analyzed by the Langmuir, Freundlich, Scatchard and Flory-Huggins isotherm models. The pseudo-first-order, pseudo-second-order, Elovich and Bangham models were used for kinetic analysis. Thermodynamics revealed a spontaneous, feasible and endothermic sorption process. The soil was found to be suitable as a low cost sorbent for tartrazine from contaminated solution.

1. Introduction

The increasing use of dyes by the paper, pulp, textile, leather, food and drug industries has led to the release of effluents containing colored substances (dyes) into the environment. Most dyes are resistant to light, temperature and oxidizers, non-biodegradable, bio-accumulate in living organisms and toxic at certain levels [1]. Tartrazine is an important dye used at very low concentrations for drugs especially for the shells of medicinal capsules, syrups, cosmetics and food additives. However it is very toxic when present in high concentrations and is highly soluble in water, which makes it difficult to identify its presence in industrial effluents [2]. High concentrations of tartrazine in humans can cause behavioral problems, such as asthma, migraines, eczema, thyroid cancer, lupus, hyperactivity and infertility [3]. The removal of such dye from effluent before discharge into water bodies is therefore important. Different methods have been utilized for dye removal which includes ozonation, microbial decomposition, coagulation/flocculation, photo-catalytic decolorization, adsorption and sono-chemical method [1]. Adsorption has been found to be

* Corresponding author.
E-mail address: kovoakpmusic@yahoo.com (K.G. Akpomie).
Peer review under responsibility of Faculty of Engineering, Alexandria University.

http://dx.doi.org/10.1016/j.aej.2016.08.008

Please cite this article in press as: M.O. Dawodu, K.G. Akpomie, Evaluating the potential of a Nigerian soil as an adsorbent for tartrazine dye: Isotherm, kinetic and thermodynamic studies, Alexandria Eng. J. (2016), http://dx.doi.org/10.1016/j.aej.2016.08.008

the most effective among the methods and activated carbon the most effective adsorbent [4]. However, the use of activated carbon is expensive which limits its widespread use, encouraging the use of cheaper alternative adsorbents such as agricultural wastes [5], sawdust [6], fly ash [7] and clay [8]. Very few works have been performed for the removal of dyes especially tartrazine from solution using soil as adsorbent [7]. This study therefore investigates the potential of soil of Nigerian origin for the removal of tartrazine from solution. The soil is present in Osun state in excess amount and can be utilized as an alternative low-cost adsorbent for sorption of tartrazine if found to be effective. The soil was utilized without any treatment or modification in order to keep the process cost low. Adsorption data were evaluated to determine the conditions of maximum sorption along with relevant isotherm, kinetic and thermodynamic equations.

2. Experimental

2.1. Characterization and sorption

The soil sample was obtained from Bowen University, Iwo, Osun state, Nigeria, and utilized without any purification. The sample was sundried for 5 days, then dried in an oven at 105 °C for 6 h, crushed and then passed through a mesh sieve of size 100 μm to obtain the prepared adsorbent.

The chemical composition of the adsorbent was determined by the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 2010VGP) after digestion of the sample with nitric and hydrofluoric acid. The pH point of zero charge (pH_{pzc}) of the soil was determined by the method described in our previous work [9]. The ammonium acetate method was used to determine the Cation Exchange Capacity (CEC) [10]. Pore properties and BET surface area were assessed via N_2 adsorption-desorption isotherms with a micromeritics ASAP 2010 model analyzer. The Fourier Transform Infrared (FTIR) spectra of the soil were obtained by the FTIR spectrophotometer (Shimadzu FTIR 8400s), while the surface morphology was assessed with the Scanning Electron Microscope (SEM) (Hitachi S4800 model).

All the reagents utilized in this study were of analytical grade, obtained from sigma-Aldrich and used without any purification. Stock solution of the anionic dye tartrazine (Acid yellow 23) with molecular formula $C_{16}H_9N_4Na_3O_9$ was prepared by dissolving appropriate amount of the dye in distilled water to obtain a concentration of 500 mg/L. Lower concentrations of tartrazine with concentrations ranging from 50 to 250 mg/L were prepared from the stock solution by serial dilution. The pH of the solutions was adjusted to values from 2 to 8 by the minute addition of 0.1 M NaOH or 0.1 M HCl when required.

Batch adsorption experiment was performed by adding 0.05 g of the adsorbent to 40 ml of a given solution in a pretreated glass bottle at room temperature of 300 K. The influence of pH (2.0–8.0), initial tartrazine concentration (50, 100, 150, 200 and 250 mg/L), adsorbent dose (0.01, 0.02, 0.03, 0.04 and 0.05 g), contact time (10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 300 min) and temperature (300, 313, 323 K) were evaluated. The bottles were placed in a thermo-stated water bath for temperature regulation when the effect of temperature was studied. In order to evaluate the effect of a particular parameter, that parameter was varied while others were kept constant at the optimum conditions of pH 2.0, contact time 120 min, tartrazine concentration 50 mg/L. At the end of a given contact time of sorption the solutions were centrifuged for 15 min at 5000 rpm. The UV–Visible spectrophotometer operating at 426 nm was then used to determine the equilibrium concentration Ce (mg/L) of tartrazine in the supernatant. The following equations were utilized in the calculation of percentage adsorption of tartrazine and the uptake capacity of the adsorbent for tartrazine respectively:

$$\%\ \text{Sorption} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{v(C_i - C_e)}{m} \tag{2}$$

where C_i (mg/L) is the initial concentration of tartrazine in solution, q_e (mg/g) is the uptake capacity, m (g) is the adsorbent dose and v (L) is the volume of solution used.

2.2. Adsorption Isotherm

The equilibrium adsorption data were evaluated by the Langmuir, Freundlich, Scatchard and Flory-Huggins isotherm models. The Langmuir isotherm describes a monolayer adsorption on a heterogeneous adsorbent surface and the linear form of the equation is expressed as [11] follows:

$$\frac{C_e}{q_e} = \frac{1}{q_L K_L} + \frac{C_e}{q_L} \tag{3}$$

where q_L (mg/g) represents the maximum monolayer adsorption capacity and K_L (L/mg) corresponds to the Langmuir adsorption constant. A dimensionless constant equilibrium parameter (R_L) gives an appropriate description of the Langmuir isotherm and is represented as [11] follows:

$$R_L = \frac{1}{[1 + K_L C_i]} \tag{4}$$

The R_L value classifies the adsorption process as favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), linear ($R_L = 1$) and unfavorable ($R_L > 1$).

The Freundlich isotherm describes a multilayer adsorption on a heterogenous adsorbent surface and the linear form of the equation is given as [12] follows:

$$\log\ q_e = \log\ K_F + [1/n] \log\ C_e \tag{5}$$

where K_F (L/g) and n are the Freundlich constants corresponding to the adsorption capacity and intensity, respectively. Values of n between 1 and 10 indicate a favorable adsorption process [13].

The Scatchard isotherm was applied to verify the homogenous or heterogonous nature of the adsorbent in comparison with the data obtained from the Langmuir and Freundlich isotherm. The linear form of the Scatchard isotherm also called independent site oriented model is expressed as [14] follows:

$$\frac{q_e}{C_e} = q_s b - q_e b \tag{6}$$

where q_S (mg/g) and b (L/mg) represent the Scatchard isotherm sorption parameters. If a straight line is obtained from the Scatchard plot of q_e/C_e against q_e, then the adsorbent presents only one type of binding site (Homogenous surface), but