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Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto *Raphia hookerie* fruit epicarp

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Highly efficient low cost adsorbent was prepared from *Raphia hookerie* fruit epicarp. Characteristics of the prepared low cost adsorbent (RH) was established using scanning electron microscope (SEM), Fourier Transform Infra Red (FTIR) and Brunauer–Emmett–Teller (BET) surface area. RH was applied for Rhodamine B (RhB) uptake from aqueous solution. Equilibrium adsorption data were fitted using four isotherms and kinetic data tested with five kinetic models. The BET surface area obtained was 0.00351 m^2/g; SEM reveals large pores that could enhance the uptake of large molecules. Freundlich isotherm best described the uptake of RhB onto RH, the maximum monolayer adsorption capacity (q_{max}) was 666.67 mg/g. Pseudo second order model best described the kinetics of adsorption process. Energy of adsorption (E) obtained from D-R isotherm suggests physical adsorption. Desorption efficiency follows the order $H_2O > HCl > CH_3COOH$. Cost analysis shows that RH is about 1143 times more economical when compared with commercial activated carbon.

1. Introduction

Textile industries generate large volume of wastewater that majorly emanate from the dye preparation, spent dye, bath and washing stages. This wastewater usually contains loads of dye molecules that are hazardous, thereby posing threats to human and other living organisms in the environment [1]. Textile industries utilize varieties of dyes such as anthraquinone based meta complex, reactive, acidic, azo, diazo, and basic. While dyeing of wool, silks, acrylic and nylon is commonly done using basic dyes, reactive dyes are better employed in other industrial dyeing processes [2]. Dyes are characterized by high molecular weight and complex chemical structures; hence, they are non-biodegradable [3].

Conventional methods of effluents treatments such as precipitation, electrochemical treatment, reverse osmosis, ion exchange, evaporation, solvent extraction, as well as adsorption with activated charcoal among others; are presently in use for the treatment of textile industrial effluent. Adsorption with activated carbon has been found to be effective because of the simplicity in its design and operation, ability to adsorb a broad range of pollutants; and fast adsorption kinetics [4]. However, the commercial activated carbon is very expensive due to the high cost of precursor, hence the quest for a more economical way of textile effluent treatment [5]. Investigations into the use of low cost adsorbent, especially bioresource

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materials as an alternative to commercial activated carbon do not only give economical advantage, it also aids environmental protection and encourages waste management. Waste materials, which naturally would have been nuisance to the environment; become useful environmental remediation tools. Lignocellulosic materials such as agricultural wastes have cellulose, hemicellulose and lignin as their basic constituents. Their polyol backbone coupled with the presence of other functional groups serve as good binding site for pollutants. Although, surface modification or functionalization may result into adsorbents with superior adsorption capacity, this however also results in decreased economic advantages [6].

Investigations into the use of various wastes as alternative low cost adsorbent for the treatment of synthetic textile industrial effluents have been widely reported. Investigation into the use of Cupuassu shells in the uptake of reactive red and direct blue dyes has been reported. Uptake of dye was more favorable in the acidic media, and equilibrium data was reported to fit best into the Sip isotherm model [7]. Removal of Ramazol black textile dye using pine fruit shell was also investigated, and reported. Acidic media also favoured the uptake of Ramozol black onto pine fruit shells, while equilibrium adsorption data fitted best into the Sip isotherm model [8]. Bello et al. [9] reported the use of ackee apple seeds in the removal of Congo Red dye from aqueous solution. Optimum adsorption was observed at pH 3. Adsorption process was fast and equilibrium was attained within 90 min. The equilibrium adsorption data fitted best into the Langmuir isotherm model. Seed husk of bangal gram was utilized for the removal of congo red, adsorption data obtained were analyzed using Langmuir isotherm, and q_{max} obtained was 41.66 mg/g [10]. Removal of Methylene blue and Eriochrome black T using Maize stem tissue has been investigated and reported. Maximum monolayer adsorption capacities were reported to be 160.84 mg/g and 167.01 mg/g for methylene blue and eriochrome black T respectively. Equilibrium adsorption data for the two dyes, was described by Freundlcih and Langmuir isotherm models [11]. The use of dika nut endocarp waste in the uptake of Rhodamine B has also been recently reported. Optimum adsorption was obtained at pH 3, equilibrium adsorption data fitted best into the Freundlich adsorption isotherm, and maximum monolayer adsorption capacity was obtained to be 212.77 mg/g [12].

Raphia hookerie belongs to the *Palmicea* family. Members of this family contain high cellulosic fibers, are good source of carbon, and have been found suitable in activated carbon preparation [13]. While other members of this family have been well explored in activated carbon preparation as well as effective low cost adsorbent [14–18], Raphia hookerie have been neglected. To the best of our knowledge, *Raphia hookerie* epicarp is yet to find applications in environmental remediation. This study therefore aimed at investigating the potential of low cost adsorbent prepared from the epicarp of *Raphia hookerie* fruit in the adsorption of a cationic dye (Rhodamine B- RhB). The physicochemical characteristics, functional groups analysis, and surface morphology of the prepared adsorbents were studied. Studies on the adsorption capacity of the biomaterial viz-a-viz kinetics, isotherms and thermodynamics analysis of the adsorption data, were carried out. The modes and mechanism of RhB uptake were well investigated and the kinetics models were validated using statistical tools. Economic advantage of the prepared adsorbent over modified biomass and commercial activated carbon are also presented.

2. Materials and methods

2.1. Adsorbent preparation

Epicarp of *Raphia hookerie* fruits were collected from local farmers in Mokogi, Edu Local Government Area of Kwara State, Nigeria. In order to remove dirts, the biomass was washed with abundant water and dried in an oven operated at 105 °C

Fig. 1. Raw *Raphia hookerie* fruit.