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Sorption dynamics and isotherm studies of methylene blue uptake on to palm kernel fibre

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Abstract

The effect of temperature on the sorption of methylene blue from aqueous solution onto palm kernel fibre has been studied. Batch kinetics and isotherm studies were performed at temperatures ranging from 299 to 339 K. The kinetic data were studied in terms of the pseudo-first-order and pseudo-second-order kinetic models and the Bangham and intraparticle diffusion models. The pseudo-second-order model best described the sorption process and was employed in predicting the rate constant, equilibrium sorption capacity and the initial sorption rate with effect of temperature. In addition activation energy of sorption has also been determined based on the pseudo-second-order rate constant. The isotherm data was analyzed by the Langmuir and Freundlich isotherms. Palm kernel fibre was found to have a Langmuir monolayer capacity of 233.41 mg g^{-1} at 299 K. The adsorption is endothermic at ambient temperature and the computation of the thermodynamic parameters, ΔH°, ΔS° and ΔG° indicates that the sorption was favourable at all temperatures.

Keywords: Palm kernel fibre; Solution temperature; Pseudo-second-order; Langmuir isotherm; Methylene blue

1. Introduction

Knowledge of the interaction at a solid–liquid interface at varying temperatures is very important in applied surface science. It is known that adsorption depends to a large extent on the surface energy interaction involved between solute and sorbent [1], therefore the equilibrium relationship between solute molecules in solution and solute molecules on the adsorbent surface will depend on solution temperature. An area of practical interest of this field is in the separation of colored substances from textile effluents. Textile effluents containing dyes are usually discharged into receiving water bodies at relatively high temperatures (50–60 °C); therefore temperature will be an important design parameter affecting the sorption of dye molecules and sorption capacity of sorbents in real application [2–4].

Basic dyes although organic, carry a positive charge on their structure and are water-soluble. They have maximum adsorption capacities that are much higher than those of acid and reactive dyes [5,6] probably due to the negatively charged surface of most adsorbents employed for effluent treatment, which possesses higher affinity for cationic dyes. Some studies have revealed that cationic dye sorption on to certain adsorbents followed ion-exchange mechanism [7–10]. Schramm et al. [11] proposed that crystal violet and ethyl violet adsorption on to montmorilonite clay occurred initially by ion exchange followed by some specific adsorption due to π electron interactions and hydrogen bonding with clay particle surface. Bhattacharyya and Sharma [12] adsorbing methylene blue on to Neem leaf powder observed that pH variation had only little effect on the amount of methylene blue sorbed. They proposed that methylene blue adsorption was due to a weak electrostatic interaction between the cationic dye and electron-rich sites of the surface of the Neem leaf powder.

Bhattacharyya and Sharma [12,13] measured the enthalpies of brilliant green and methylene blue dyes on to Neem leaf powder. They found that the enthalpies of adsorption of both brilliant green and methylene blue dyes on to Neem leaf powder are endothermic for all amounts adsorbed. Rytwo and Ruiz-Hitzky [14] sorbing crystal violet and methylene blue on to montmorilonite clay, found that the enthalpy of adsorption of crystal violet is exothermic for all amounts adsorbed, while the enthalpy of adsorption of methylene blue is either exothermic or endothermic, depending on the extent of loading. A comparison of the

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Table 1
The maximum sorption capacities (mg g^{-1}) of methylene blue of various sorbents

Sorbent	q_m (mg g^{-1})	Reference
Natural clay	300	[15]
Cotton waste	240	[16]
Chemviron	238	[17]
Coal	230	[16]
Hair	120	[16]
Water hyacinth	128.9	[18]
Coconut husk	99	[19]
Activated carbon (CEA 40)	370	[20]
Palm kernel fibre	223.41	This study

sorption capacities of different sorbents for methylene blue is given in Table 1.

This study is aimed at investigating the effect of varying temperature on the kinetics and equilibrium uptake of methylene blue dye from aqueous solution on to palm kernel fibre. The pseudo-first- and pseudo-second-order kinetic models and Bangham and intraparticle diffusion models were employed to analyze the kinetic data on the effect of temperature. The feasibility of the application of palm kernel fibre as adsorbent at the temperature range at which textile effluents are discharged was also investigated.

2. Experimental

2.1. Materials

Palm kernel fiber used in this study was obtained from the Nigerian Institute for Oil Palm Research (NIFOR), Benin City, Nigeria. The palm kernel fiber was allowed to dry with the residual oil, after processing for about 2 months. The raw fiber was dried in an oven at 80 °C for 6 h, grounded and screened through a set of sieves to obtain particles of size 50–60 μm. The sieved fiber was steeped in 0.02 mol L^{-1} HCl overnight. The acid solution was filtered off and the fiber washed with distilled water until the pH of the wash becomes neutral. The fiber was dried at 80 °C for 24 h and stored in an air-tight container.

The basic dye, methylene blue (BDH, 85% dye content) was used without further purification. The stock solution of 1000 mg L^{-1} was prepared by dissolving 1.127 g methylene blue in 1000 mL distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.2. Methods

2.2.1. Some characteristics of palm kernel fibre

The proximate composition of the palm kernel fibre was determined using the Association of Official Analytical Chemist (AOAC) [21]. Lipid content was determined using solvent extraction method with petroleum ether; moisture content was determined by thermal drying method at 105 °C; ash content was determined by ignition method; protein content was by the determination of the total organic nitrogen using the macro kjeldhal method and then converting to crude protein, while fibre content was determined by ashing at 500 °C for 3 h.

The IR spectra of the palm kernel fibre sample were recorded using KBr disk in conjunction with a Perkin-Elmer infrared spectrophotometer having resolution of 4 cm^{-1} and range between 4000 and 400 cm^{-1}. KBr disk were prepared by mixing a given sample with KBr crystals, the resulting mixture being ground to a fine powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr disk under vacuum conditions and used as such for IR studies.

2.2.1.1. Theory. Sorption in a methylene blue/palm kernel fibre system results in the transfer of methylene blue to the surface of the palm kernel fibre, where it increases in concentration until a dynamic equilibrium is reached between palm kernel fibre and methylene blue remaining in the liquid phase. These characters of biomaterials can be involved in chemical bonding and are responsible for their cation exchange capacity. Thus, the reaction may be expressed by the following two relationships [22–24]:

$$F^- + MB^+ \rightarrow MBF \quad (1)$$

and

$$2HF + (MB)_2{}^{2+} \rightarrow 2MBF + 2H^+ \quad (2)$$

where F^- and HF are polar sites on the palm kernel fibre surface.

The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of palm kernel fibre and the amount sorbed at equilibrium.

The rate expression for the sorption described is

$$\frac{d(F)_t}{dt} = k[(F)_0 - (F)_t]^2 \quad (3)$$

or

$$\frac{d(HF)_t}{dt} = k[(HF)_0 - (HF)_t]^2 \quad (4)$$

where $(F)_t$ and $(HF)_t$ are the number of active sites occupied on the palm kernel fibre at time t and $(F)_0$ and $(HF)_0$ are the number of equilibrium sites available on the palm kernel fibre. The kinetic rate equations can be rewritten as follows

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 is the rate constant of sorption (g mg^{-1} min^{-1}), q_e the amount of lead ions sorbed at equilibrium (mg g^{-1}) and q_t is the amount of lead ions sorbed on the surface of the palm kernel fibre at any time t (mg g^{-1}).

Separating the variables in Eq. (5):

$$\frac{dq_t}{(q_e - q_t)^2} = k\,dt \quad (6)$$

integrating this for the boundary conditions $t = 0$ to t and $q_t = 0$ to qt, gives

$$\frac{1}{(q_e - q_t)^2} = \frac{1}{q_e} + kt \quad (7)$$