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Kinetics investigation and Equilibrium studies on the biosorption Leuco-form of Indigo Blue dye using chemically modified Coconut fibre

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Abstract

In recent years, cheaply available agricultural wastes are increasingly finding useful applications in environmentally friendly ways. In this study, we investigate the effectiveness of the use of chemically modified coconut fibre in the biosorption of indigo blue dye from its solution. The influence of the variation of pH, contact time, concentration of dye and biosorbent dose on the biosorption process as well as the kinetics of the sorption process was studied. The biosorption equilibrium data were analysed with Langmuir, Freundlich and Temkin isotherms. The results showed that there was maximum percentage dye removal of 94.64 % at pH 6 within contact time of 1 hr. Similarly, 80 mg/L of biosorbent dosage and 0.05 mg/L of initial dye concentration gave the maximum percentage dye removal of 86.43 % and 95 % respectively. The Langmuir isotherm with R^2 value of 0.9963 was the best model to describe the equilibrium data and the biosorption process followed the pseudo second order kinetics with a rate constant k_2 value of 1.20 $gmg^{-1}min^{-1}$ at the initial dye concentration of 0.05 mg/L. Therefore, the chemically modified coconut fibre is shown a suitable low cost biosorbent for the treatment of indigo dye effluents.

Keyword: Coconut fibre, Biosorbent, Indigo blue, Isotherm, pseudo second order

1. Introduction

Textile processing industries majorly uses both natural and synthetic dyes as a colouring material. The effluents from dyeing and desizing processes of these textile industries contributes to the high colourant content and chemical oxygen demand of the receiving water bodies (Grof *et al.,* 1989). Many of these dyes have large molecular size and complex structures. They are mostly non-oxidizable substances because of their stability to light and oxidation processes (Moran *et al.,* 1997). Therefore, effluents from these textile industries require pretreatment prior to disposal into receiving water bodies.

Indigo blue dye is among the commonly used dye in the textile industries. It's one of the

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oldest dyes used by mankind. Indigo dye works by oxidation-reduction process (redox reaction). Naturally occurring indigo is insoluble in water; it is converted to the water-soluble form by reducing it in the presence of alkali such as sodium hydrosulphite, thiourea dioxide (thiox), zinc or bacteria which acts as a reducing agent. After reduction, the water-soluble indigo blue becomes colourless and has high affinity for cellulosic fibers, penetrating all the holes in the fiber (Li, 1987; Hoessel *et al.*, 1999; Stasiak *et al.*, 2014 and Wang *et al.*, 1984). When the dyed fibers are exposed to air, the dye molecules oxidize back to the blue coloured insoluble form trapped within the fiber, thereby colouring them permanently blue. The interaction between indigo and fabrics is mechanical and not chemical bond formed by other dyes (Sollars *et al.*, 2001).

Industrial effluents need to be treated before discharge to the water bodies. The commonly employed methods for the treatment of effluents include chemical precipitation, electrochemical treatment, chemical oxidation or reduction, filtration, ion exchange, membrane technologies, evaporative recovery and adsorption. Among the different treatment methods, the adsorption technique, standout as a simple but efficient method for removing contaminants from the water. Adsorption has been effectively employed in the treatment of industrial effluents, removal from dye wastewater and a valuable device for reclaiming nature (Crini, 2006; Grupta and Suhas, 2009; Ramakrishna and Viraraghavan, 1997; Saikia *et al.*, 2017 and Sandanand and James, 2016). In recent times, biological methods such as biosorption, bioaccumulation or bioremediation are becoming a more attractive alternative for effluent treatment (Crini, 2006; Grupta and Suhas, 2009 and Ramakrishna and Viraraghavan, 1997). Biosorption is the use of agricultural wastes and dead micro-organisms in pretreated and immobilized forms for adsorption processes. These materials are environmentally friendly, cheaply available and possess numerous binding sites for the adsorbate molecules (Raghavacharya, 1997).

Coconut husk is a readily available agricultural waste that can be mechanically converted into a fiber form by pulverization. The coconut fibre has been reported to be largely made up of cellulose, hemicellulose, pectin, lignin and different minerals (Etim *et al.*, 2016). These properties of the coconut fiber are the basis for its uses in the preparing different types of composites, such as natural adsorbents, bioplastics and other raw materials used for several industrial processes.

This study investigates the optimum conditions for the application of chemically modified coconut fibre in the biosorption of indigo blue dye in aqueous medium. The kinetics of the biosorption process and the isotherm model that best describe the equilibrium data were also determined.

2. Materials and Methods

2.1. Apparatus and Reagents

Measuring cylinder, standard conical flasks, Volumetric flasks, Pipette, Burette, filter paper, funnel, paper tape, pH meter (Searchtech PHS–3C), Weighing balance (S. Mettler analytical balance), water bath shaker (Searchtech SHZ-82), UV-Visible spectrophotometer (Beckman coulter DU 730).

The biosorbent, coconut fibre was sourced from a coconut processing mill in Ikeja, Lagos state, Nigeria. Crude Indigo blue dye was purchased from a local market in Abeokuta, Ogun state, Nigeria. Indigo blue has molecular formula $C_{16}H_{10}N_2O_2$ (Mol. wt. 262.27 g/mol). The crude indigo dye was reduced to its water-soluble form for the sake of the experiment. Reagents for reduction of the dye are sodium thiosulphate ($Na_2S_2O_4$) and dilute 3M NaOH solutions. All the reagents used were of analytical grade from BDH chemicals.

2.2. Modification of Biosorbent (Coconut Fibre)

The Coconut fibre was modified in a three-step procedure of (Arsyad *et al.*, 2015) to obtain the chemically modified fibre. The reagents for coconut fiber's surface treatment were aqueous solutions of 5 – 20 % *w/v* NaOH, 0.25 – 1 % $KMnO_4$ and 5 – 20 % *w/v* H_2O_2. The coconut fibre was firstly treated with the NaOH solution, then with the $KMnO_4$ solution and finally with the H_2O_2 solution, oven dried at 90 ^oC and cooled to room temperature. This chemically modified fibre was then air- dried, pulverized and sieved to 500 μm size.

2.3. Characterization of the Biosorbent (Coconut Fibre)

2.3.1 Fourier Transform Infra Red (FTIR) Spectroscopic Analysis

The FTIR was used to determine the nature and types of functional groups present in the biosorbent. The pulverized crude biosorbent and the used biosorbent after the biosorption process were analysed using the Schimadzu IRAffinity-1S spectrophotometer.

2.3.2. Scanning Electron Microscope (SEM) Analysis

The morphology of the biosorbent before and after the biosorption process was investigated using SEM machine (Vega3 Tescan). Samples were attached to the aluminum stubs and then examined using an accelerating voltage of 3.0 kV

2.4 Preparation of Stock solution of the Dye

The leuco-soluble form (Figure 1) of indigo blue dye used for the experiment was prepared by weighing 0.02 g of crude Indigo dye and 0.12 g of $Na_2S_2O_4$ into a beaker of 50 ml of de-ionized water, then, 1.2 ml of 3 M NaOH solution was added. The solution obtained was gently warmed to a temperature of 50 ^oC until its green colour changed to blue (Fernelius and Renfrew, 1983). The resulting blue solution was made up to mark in a 100 ml volumetric flask to prepare give 0.2 g/L stock solution of the dye. The experimental concentrations of 0.4, 0.8, 1.2, 1.6 and 2.0 mg/L were then prepared from the stock solution by serial dilution.

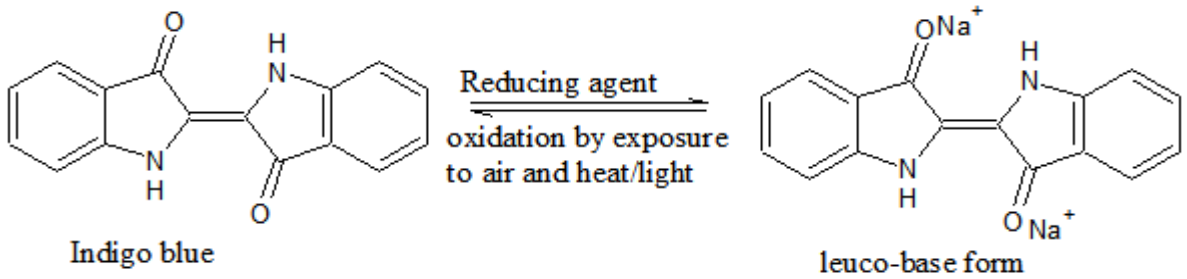

Figure 1: Reduction of insoluble Indigo blue to soluble leuco-base form of Indigo blue.

2.5 Biosorption Experiment

20 ml of 0.2 mg/L dye solution was agitated with 50 mg of the chemically modified coconut fibre (except for effect of biosorbent dose, where the mass of fibre was varied) at a constant speed of 200 rpm for 3 hours in a shaker after which they were centrifuged at 4,000 rpm for 20 minutes to separate the supernatant. The experiments were carried out in triplicate after which 5 ml of each supernatant is taken and analyzed for the residual dye content with UV – Visible Spectrophotometer (Beckman coulter DU 730) using a λ_{max} of 640 nm. 0.05 – 0.3 mg/L dye concentrations were used to investigate the influence of variation of initial dye concentrations on the biosorption process. The pH ranges of 2 – 8 were used for influence of pH on the biosorption. The influence of contact time was investigated at the time range of 3 – 7 hours contact time while for the biosorbent dose, 10 –150 mg of biosorbent was used.

The equilibrium concentration (q_e) for the biosorption process was determined as:

$$q_e = \frac{(C_o - C_e)\,V}{W}, \quad (1)$$

where C_o = initial dye concentration (mg/L), C_e = equilibrium dye concentration (mg/L),

V = volume of the dye solution (L) and W = weight (g) of the biosorbent. The extent of dye removal for each of the batch process was determined in percentage as:

$$\%\ dye\ removal = \frac{C_o - C_e}{C_o}\ x\ 100. \quad (2)$$

3. Result and Discussion

3.1 Characterization of the Biosorbent

3.1.1 FTIR Spectroscopic Analysis

The FTIR spectrum of the modified coconut fibre (Figure 2) exhibits a broad peak at 3437 cm^{-1}, which is characteristic of the stretching vibrations of O–H bonds in components like cellulose, hemicellulose, pectin, and lignin. Free and bonded O–H bands of carboxyl group were observed as the O – H stretching vibrations occurred within a broad range of frequencies. The presence C–H stretching vibration band of methylene, methyl- and methoxy- groups can be attributed to the peak at 2356 cm^{-1}. The peak observed at 1639 cm^{-1} is the stretching vibration attributed to non-ionic –COOR and may be due to the presence of organic acids or their esters. The symmetric stretching vibrations of the C=O in the COOR group is observed at 1620 cm^{-1}, while the peak at 1026 cm^{-1} is due to symmetric stretching of $-COO^-$ group. The FTIR spectra reveal that the chemically modified coconut fibre possesses many active functional groups that serve as exchanging sites for the biosorption process.

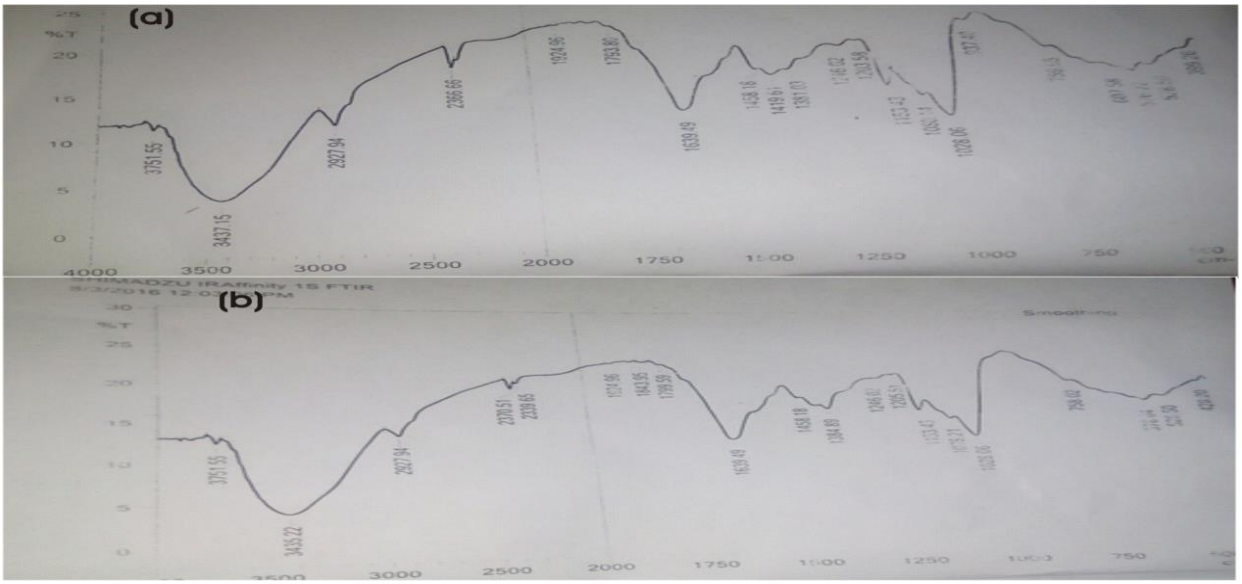

Figure 2: FTIR result of the modified coconut fibre (a) before and (b) after biosorption of Indigo blue dye

3.1.2. Scanning Electron Microscope Analysis

The SEM image of the modified coconut fibre was taken before and after the biosorption experiment to reveal the morphology of the biosorbent's surface and how it affects the biosorption process. Figure 3 shows the SEM micrographs at 50 µm and 500 µm magnifications. The micrographs the modified coconut fibre before biosorption (Figures 3a and 3b) reveal a dispersive surface with coagulated/lumped-up particles separated by pores of different sizes. This may be attributed to the effect of NaOH solution used for modification. The coagulated particles and varying pore sizes of coconut fibre implies the surface possess the needed sites for the biosorption process. Figures 3c and 3d are the SEM micrographs for the modified coconut fibre after the biosorption process at 50 µm and 500 µm magnifications respectively. The surface appears to be smooth and regular indicating that fibre pores have been filled with dye molecules and are no longer visible.

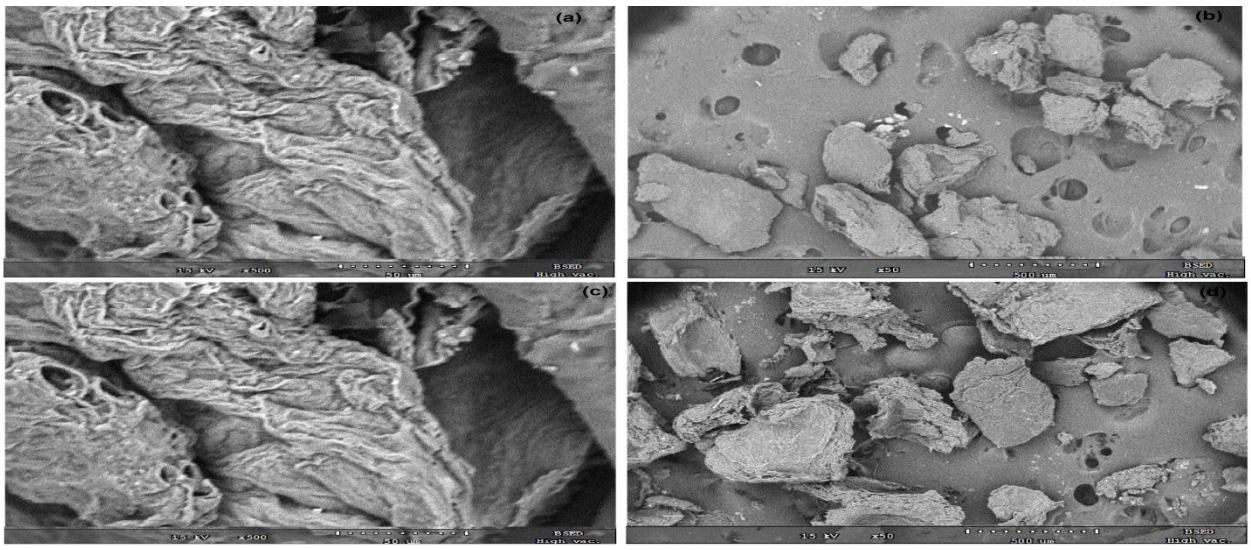

Figure 3: Scanning Electron Micrograph of the crude Coconut fibre at (a) x 50µm and (b) x 500 µm magnifications, (c) x 50µm and (d) x 500 µm magnifications after biosorption process.

3.2. Biosorption Experiment

3.2.1. Variation of pH

Figure 4a shows the influence of pH on the biosorption process. The aqueous solution of the dye had an initial basic pH value 11. The highest uptake of the dye occurred at pH of 6 with percentage dye removal of 96.4 %. This is expected because at acidic pH, there is reduction in the OH^- ions present in the medium to compete with those on the dye molecule for the

available sites on the biosorbent surface. As reveal from the FTIR result, the coconut fibre consist more of acidic functional groups, hence, biosorption process should be more favourable at acidic pH at which the acidic groups on the fibre exert increased electrostatic force on the hydroxyl groups of the dye molecules. This explains the gradual increase in the percentage dye removal till pH value of 6 before the eventual decrease in percentage dye removal.

3.2.2. Variation of biosorbent dose

There is an initial in percentages of dye removal as the adsorbent dosage increases from 10 mg to 80 mg, at which percentage dye removal is 86.43 (Figure 4b). As the biosorbent dosage is increased, there is increase in surface area and the hence adsorption sites. There is however gradual decrease in percentage dye removal as the biosorbent dosage exceeds 80 mg. This may be attributed to overlapping of adsorption sites available to the dye due to limited volume of the biosorption.

3.2.3. Variation of Initial dye Concentration

The percentage dye removal decreased with increase in the initial concentration of the dye (Figure 4c). The lowest initial dye concentration has the highest percentage of dye removal. This means that the optimum concentration for the bisorption process with the dosage of coconut fibre used is the lowest concentration (0.05 mg/L). Bulut and Aydin, 2006, attributed increase in the loading capacity of the biosorbent to the high driving force for mass at the initial dye concentration. Therefore, the concentration with the highest driving force with a given biosorbent will favour the biosorption process the most. The inter play between adsorption sites available on the biosorbent and the initial number of dye molecules regulates the driving force.

3.2.4. Variation of Contact time

The optimum removal of indigo dye from aqueous solution by coconut fibre was achieved at contact time of 1 hour (Figure 4d). There was irregular but gradual reduction in the percentage dye removal as the contact increases above 1 hour. This means that the rate of biosorption process was initially very fast and the available binding sites of the biosorbent were readily filled within one hour of contact but as the contact time is increased there is a shift in the partition of the dye molecule between the bisorbent and the aqueous medium. The

decrease in percentage dye removal may be due to the fact that the biosorption process favoured monolayer saturation of the biosrbent surface.

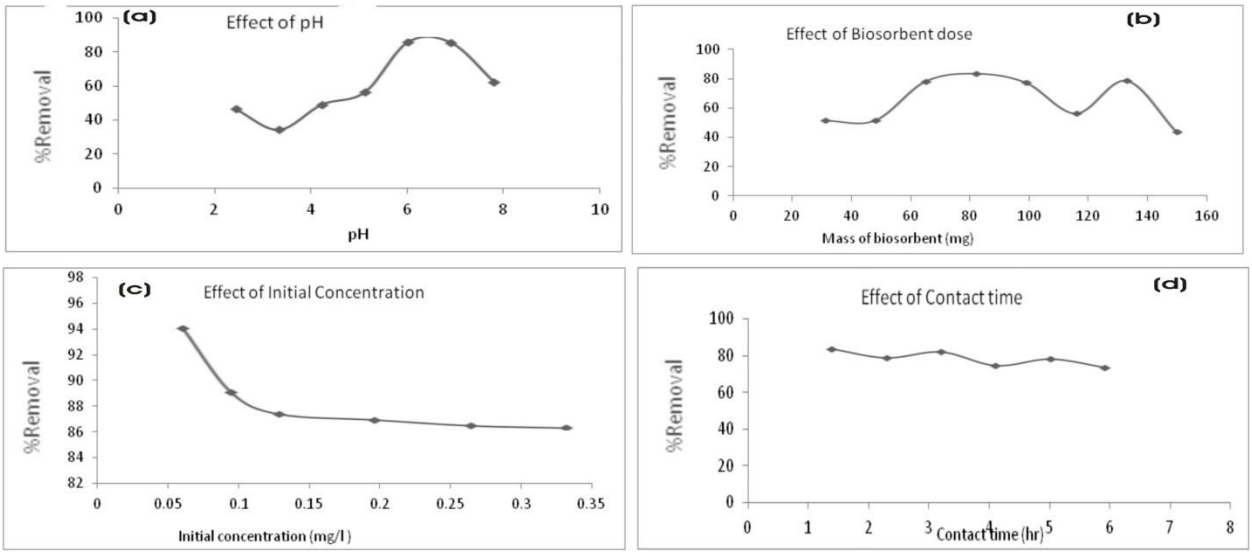

Figure 4: Plots of variation of (a) pH (b) biosorbent dose (c) Initial dye concentration (d) time; on the biosorption of indigo dye by coconut fibre from aqueous solution.

3.3 Adsorption Isotherms

3.3.1 Langmuir Isotherm

The Langmuir isotherm model (Langmuir, 1918) describes the monolayer adsorption of a solute from aqueous solution to a biosorbent with finite number of binding sites.

Langmuir model is expressed in linear form (Dabrowski, 2001) as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}, \quad (3)$$

where $C_e$and q_e are the concentration of the dye in solution (mg/L) and the amount of dye adsorbed (mg/g) respectively at equilibrium time. $q_{max}$and K_L are Langmuir constants for maximum biosorption capacity (mg/g) and energy of biosorption (L/mg) respectively. The values of q_{max} and K_L for the biosorption of indigo blue dye are obtained from the slope and intercept respectively of the plot of $\frac{C_e}{q_e}$ versus C_e shown in Figure 5a.

The main characteristic of the biosorption process is determined from the Langmuir isotherm as separation factor; R_L, a dimensionless constant (Ayawei et *al.*, 2015) given by the expression:

$$R_L = \frac{1}{1+K_L C_o}. \quad (4)$$

When, R_L > 1, the biosorption is unfavourable, when R_L = 1, it is linear, when 0 < R_L <1, it is favourable and when R_L = 0, it is irreversible.

3.3.2 Freundlich Isotherm

The Freundlich isotherm model (Freundlich, 1906) is used to describe multilayered adsorption on heterogeneous surface of biosorbent. It explains the nature of interaction between adsorbate and the active sites on a surface in which the heat of sorption is heterogenously distributed. Freundlich model is expressed in linear form (Boparai *et al.*, 2011) as:

$$Log\ q_e = LogK_F + \frac{1}{n} Log\ C_e, \quad (5)$$

where $C_e$and q_e are the concentration of the dye in solution (mg/L) and the amount of dye adsorbed (mg/g) respectively at equilibrium time. K_F and *n* are Freundlich isotherm constants indicating the biosorption capacity and a measure of the biosorption's deviation from linearity respectively. *n* is used to determine the types of biosorption process (Crini and Badot, 2008), when *n* =1; the biosorption is linear, but when *n* < 1, the biosorption is a chemical process, and when *n* > 1 the biosorption process is thermodynamically favourable. The value of *n* is the reciprocal of the slope obtained from the plot of $Log\ q_e$ against $Log\ C_e$ (Figure 5b).

3.3.3 Temkin

The Temkin isotherm model (Temkin and Pyzhev, 1940) describes the nature of the adsorbate – adsorbent interactions. It proposed a uniform distribution of binding energies for the available number of the binding sites on the bisorbent surface. The Temkin isotherm is expressed in linear form (Vijayaraghavan *et al*., 2006) as:

$$q_e = \frac{RT}{b} K_T + \frac{RT}{b} InC_e, \quad (6)$$

where *b* and K_T are the Temkin constants relating to the heat of adsorption ($Jmol^{-1}$) and binding adsorption at equilibrium (L/mg) respectively. The quantity $\frac{RT}{b}$ is given as the Temkin constant B_1, B_1 and K_T values are determined from the slope and intercepts of the plot of q_e against $ln\ C_e$, (Figure 5c).

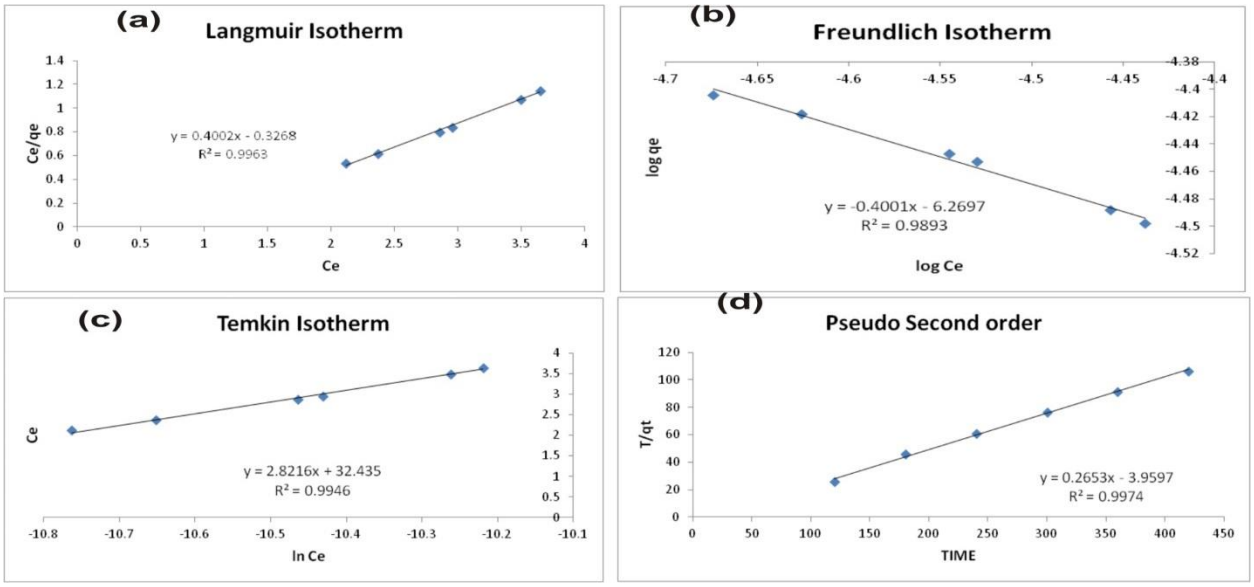

Figure 5: Isotherm plots for the biosorption of indigo dye onto modified coconut fibre at 25 ºC (a) Langmuir, (b) Fredluich (c) Temkin and (d) Pseudo-second order Kinetic plot of biosorption process.

Table 1: Values of the adsorption isotherm parameters obtained from biosorption of indigo dye by coconut fibre.

Isotherm models	**Parameters**	**Value**
Langmuir	q_{max}	3.71
	K_L	-0.68
	R^2	0.9963
	R_L	0.075
Freundlich	n	-2.64
	K_F	3.14 x 10^{-5}
	R^2	0.9893
Temkin	B_1	2.14
	K_T	0.55
	R^2	0.9946

3.4. Biosorption Equilibrium kinetics

The pseudo-second-order kinetic model (Blanchard *et al.*, 1984) has been successfully used to describe physiosorption and chemisorption processes. This kinetic model can be used to predict the biosorption process for all dye concentrations since it is based on the adsorption capacity of the biosorbent. The pseudo-second order kinetic model is given by the expression (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t, \qquad (7)$$

where K_2 is the pseudo-second order rate constant for the biosorption ($gmg^{-1}min^{-1}$). The pseudo-second order plot at the six initial dye concentrations for the biosorption process is

shown in Fig. 5d. The values of $q_e and\ K_2$ as obtained from the slopes and intercepts respectively at different dye concentrations are presented in Table 2. There is a perfect fit of the process to the pseudo second-order kinetic model because the correlation coefficient (R^2) value for the range of dye concentrations investiagted was approximately equal to 1.

Table 2: Pseudo second order Kinetic parameters for biosorption of indigo dye by coconut fibre.

Conc. (mg/l)	$q_{e,\exp}\ (mg/l)$	$q_e\ (mg/g)$	$K_2\ (g/mgmin)$	$q_{e,calc}(mg/l)$	$q_{e,calc)}(mg/g)$	R^2
0.05	0.082	9.79	1.20	0.081	9.98	0.9974
0.07	0.079	9.70	2.00	0.079	9.85	0.9969
0.1	0.077	9.50	5.88	0.076	9.72	0.9965
0.2	0.076	9.20	8.54	0.074	9.51	0.9965
0.25	0.076	8.00	20.00	0.073	8.54	0.9962
0.30	0.076	6.80	25.00	0.075	7.12	0.9963

4. Conclusion

The findings from this study established the usefulness and efficiency of a hitherto agricultural waste, coconut fibre for the biosorption of indigo dye from aqueous medium and by extension, from effluents. Although, the best fitted equilibrium model for the biosorption process is the Langmuir isotherm, the three adsorption isotherms used for the equilibrium data were able to successfully describe the biosorption process with linear correlation coefficients approximately equal to 1. The experimental data were described by the pseudo-second order kinetic model.

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