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**Optimization of Biosorprive Removal of Dichlorvos Removal from Synthetic Wastewater by Acid-Activated *Tithonia diversifolia* Xylem**

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**Abstract**

The study examined the suitability of Activated *Tithonia diversifolia* xylem (ADFX) as a biosorbent for removal of Dichlorvos. *Tithonia diversifolia* xylem (TDFX) was activated in an acidic medium before biosorption to increase the surface area. The ADFX before and after biosorption were characterized using Fourier Transform Infrared Spectrometer (FTIR). Biosorption of Dichlorvos was optimized using the D-optimal Design and the factors selected include the contact time (60-120 min), initial concentration of Dichlorvos solution (50-200 mg/L), and the biosorbent dosage (0.2-0.6 g). The optimization studies were analysed using statistical tools included in the Design Expert software. Appropriate isotherm, kinetics, diffusion models, and thermodynamics that best describe the biosorption mechanism were determined. The FTIR spectra show change in absorption peak before and after biosorption. The optimum values obtained for the adsorption capacity and percentage removal are 0.3382 mg/g and 51.04% at 60.07 min contact time, 200 mg/L initial concentration of Dichlorvos solution and 0.20g biosorbent dosage. The process fitted best with Freundlich isotherm (R2 = 0.9998), Elovich kinetics model (R2 = 0.9730, 0.9454, and 0.8991 at 30, 40, and 50 mg/L initial concentration of the Dichlorvos) while the particle diffusion (Webber-Morris diffusion) was the rate-controlling step. The thermodynamic analysis indicates the process was endothermic with decreasing degree of disorderliness.

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1. **Introduction**

Organophosphate pesticides including Dichlorvos (2,2-dichlorovinyl dimethyl phosphate), are among the most widely utilized insecticides, especially in agriculture and around 50% of all pesticides developed and used generally belong to this group [1]. The highly intense and common usage of pesticides has resulted in considerable freshwater poisoning by these substances [2,3]. Purifying pesticide-contaminated water has been an essential environmental exercise [4]. Conventional water purification methods, however, cannot remove many of these organic chemicals [5]. There are several approaches to eliminating pesticides from aqueous solutions, including oxidation [6] Photocatalysis [7,8], electrochemical, and adsorption [9]. Biosorption is a physicochemical mechanism through which biological materials are used to adsorb unwanted molecules (pollutants) in a solution. The process has several advantages such as being widely available in nature, inexpensive, versatile, effective, and reusability. Biosorption efficacy depends on multiple factors such as contaminant chemical composition, ionic strength, the nature of the biosorbent, and pH. Nowadays, most of the research is aimed at utilizing effective, widely obtainable, and inexpensive precursors such as *tithonia diversifolia* (Sunflower) xylem as biosorbent.

The study presents the use of *tithonia diversifolia* xylem (TDFX) as an absorbent for Dichlorvos pesticide removal from an aqueous solution. The TDFX was activated using acetic acid, and the activated *tithonia diversifolia* xylem (ADFX) was characterized before and after biosorption. The experiment for the biosorption process was designed using D-optimal Design under Response Surface methodology (Design Expert v7.0) and the influence of adsorption factors such as the contact time, and initial concentration of the Dichlorvos, and biosorbent dosage on adsorption capacity and percentage removal were studied. The adsorption isotherm, kinetics, diffusion mechanism, and thermodynamic properties were also examined.

**2. Methodology**

The natural precursor used for this study was *Tithonia diversifolia* Xylem, The reagent used include Dichlorvos, distilled water, and acetic acid. The equipment used includes Ultraviolet-visible spectrophotometer (UV752D), Fourier Transform Infrared Spectrometer (BUCK FTIR SPEC), Rotary shaker (HZ 300), Electric oven (Saisho, S936), weighing balance (ZC20602), Magnetic Stirrer and Centrifuge, Bench-top blender, Mechanical sieve shaker

***2.1. Preparation of biosorbent***

***2.1.1. Material pre-treatment***

The stems of the *Tithonia diversifolia* plant were harvested from uncultivated land. The stems were broken and *Tithonia diversifolia* xylems (TDFX) were separated, and cleaned with distilled water to eliminate contaminants. They were sun-dried for 72 hrs and then dried in an oven to constant weight. The material was ground and screened to achieve a uniform size. The pulverized TDFX was stored in a sealed polythene bag for the further activation process.

***2.1.2. Activation of the biosorbent***

TDFX was activated in an acidic medium in order to increase the surface area for biosorption. The pulverized TDFX was soaked with excess 2 M of acetic acid for 24 h at an impregnation ratio of 5 g/100 ml [10]. The 2 M of the acetic acid solution was prepared by dissolving 30 g of it in 1 L of distilled water. The mixture was thoroughly mixed and heated at 100oC until it forms a paste. The paste was allowed to cool at ambient temperature and 0.1 M of NaOH was added before being washed several times with distilled water until the pH was 7. It was further dried at 60oC in an oven for 48 h. The activated biosorbent (ADFX) obtained was also kept in a sealed polythene bag until it was used as a biosorbent.

***2.2. Characterization of ADFX***

FTIR was utilized to establish the functional group present in ADFX before biosorption and after interacting with the adsorbate (DDVP). The samples were prepared by incorporating ADFX and potassium bromide (1:10) and further pressing them into a pelletized disc. The FTIR spectra were measured from 400 to 4000 cm-1 [11].

***2.3. Preparation of synthetic wastewater***

Dichlorvos solution (50 mg/L) was prepared by dissolving 50 mg in 250 ml of distilled water in a standard volumetric flask. For complete dissolution of the Dichlorvos, the mixture was thoroughly shaken and distilled water was added to level it up to 1000 ml. The procedure was repeated to prepare 100, 150, 200, and 250 mg/L of Dichlorvos solution.

***2.4. Batch biosorption experiment***

A batch adsorption study was conducted by mixing 1 g of ADFX with 100 ml of 50 mg/L solutions of Dichlorvos inside 250 ml conical flask at ambient temperature, in order to assess the biosorption effectiveness of the ADFX. The mixture was agitated at 150 rpm using a rotary shaker for a preset time. The solution was centrifuged at 1500 rpm for 30 min, during which the precipitate formed was decanted and analysed at a wavelength of 214 nm using a UV-vis spectrophotometer. The process was repeated for 100, 150, 200, and 250 mg/L Dichlorvos solution. The adsorption capacity and percentage removal were measured using Eqn 1 and 2, respectively.

(1)

(2)

***2.5. Experimental design***

The D-optimal design was used in optimizing the experimental runs for the adsorption of Dichlorvos onto the ADFX. The factors selected for the study were the initial concentration of the Dichlorvos solution (), Biosorbent dosage (), and contact time (tc) while the responses to be determined were adsorption capacity (mg/g) and the percentage removal (%). The experiments were conducted with within the range 50-200 mg/L, tc between 60-120 min and *B*d between 0.2-0.6 g. The experiment was carried out at ambient temperature with constant pH and agitation rates of 7.0 and 150 rpm, respectively. The Design Expert (7.0.1) software generated eighteen (18) experimental runs for the D-optimal design. The best model that has the highest order of polynomial with significant added terms without aliased was selected. The fitness of the models was ascertained based on the square of their corresponding correlation coefficient (R2).

***2.6. Effect of Adsorption Factors***

The effect of tc was analysed by varying tc between 15 to 240 min with 1.0 g *B*d, and between 30-50 mg/L at a constant agitation rate of 180 rpm. The resulting mixture was centrifuged at 1500 rpm and ambient temperature for 15 min, while a UV-Vis spectrophotometer was used to examine the supernatant collected. Furthermore, the influence of *B*d on the biosorption of Dichlorvos was studied by varying *B*d dosage between 0.1 - 0.6 g with between 30-50 mg/L at an agitation rate of 180 rpm for 90 min. The resulting mixture was also centrifuged at 1500 rpm for 15 min, while a UV-Vis spectrophotometer was used to examine the supernatant collected. Finally, the effect of temperature on the biosorption process was studied by varying temperature (*T*p) between 30-60 °C and the tc between 20-120 min and 50 mg/L at a constant agitation rate of 120 rpm. The mixture was centrifuged at 1500 rpm for 15 min at ambient temperature and the supernatant was analysed using a UV-Vis spectrophotometer.

***2.7. Adsorption isotherms***

Adsorption isotherms provide essential information stating the biosorbent correlation at constant temperature and concentration. Specified models were fitted to the adsorption data and investigated to identify the best fit for the study. The coefficient of determination (R2) of the models was evaluated to determine the suitable isotherm. The linearized form of the models and the variables plotted are presented in Table 1.

Table 1: Selected isotherm models

|  |  |  |
| --- | --- | --- |
| **Isotherms** | **model equations** | **variables plotted** |
| Langmuir |  |  |
| Freundlich |  |  |
| Harkins-Jura |  |  |
| Dubinin-Radushkevich |  |  |

***2.8. Kinetics and diffusion study***

Kinetic studies help determine the mechanisms that govern the Dichlorvos biosorption. The pseudo first-order (PFO), pseudo second-order (PSO), Elovich models, and diffusion models (Webber-Morris, Dumwald-Wagner, and McKay film diffusion) were fitted to the experimental data obtained. The linearized form of the kinetic models and the variables plotted are presented in Table 2.

Table 2: Selected kinetics and diffusion study

|  |  |  |
| --- | --- | --- |
| **Kinetics Models** | | |
| **Models** | **Model equation** | **Variables plotted** |
| Pseudo-first-order |  |  |
| Pseudo-second-order |  |  |
| Elovich |  |  |
| **Diffusion Models** | | |
| Webber-Morris |  |  |
| Dumwald-Wagner |  |  |
| McKay film diffusion |  |  |
|  | | |

***2.9. Thermodynamics study***

The influence of temperature was further studied as a significant parameter influencing the adsorption potential of ADFX and the kinetic mechanism of Dichlorvos biosorption. The adsorption tests were performed at elevated temperatures of 303-333K and the data obtained were used to measure the thermodynamic parameters. The three major thermodynamics parameters examined were ∆Hº, ∆Sº, and ∆Gº, calculated using Eqn. 3 – 6:

(3)

(4)

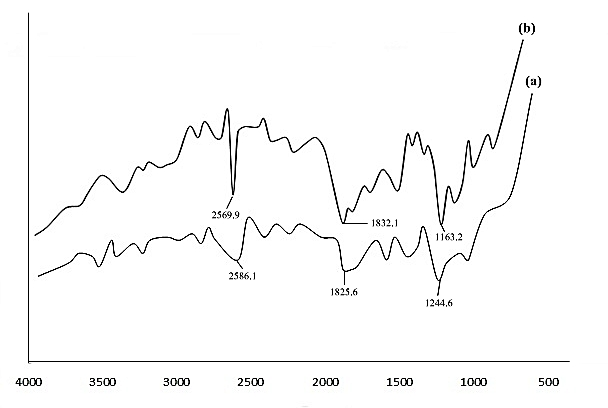
(5)

(6)

**3. Results and discussion**

* 1. ***FTIR Analysis***

The FTIR spectra of the ADFX before and after biosorption are presented in Figure 1. The IR peaks before biosorption range from 607.9-3911.3 cm-1 while the IR peak after biosorption ranges from 607.7-3931.9 cm-1. There was a significant reduction in peak height after biosorption. This was attributed to the breakdown of intermolecular bonding that occurred during the molecular interaction of the functional groups during the activation of the biosorbent [12]. The FTIR spectra revealed the presence of Alkyl halides (C-Cl, C-Br, and C-F), Amine (N-H), Alkenes (C=C), Alkyne (C≡C), Alcohol (O-H), Aldehyde (C=O, =C-H), and Ester (C-O) before and after biosorption. The absorption band of 2569.9 cm-1 (Figure1b) was due to the O-H stretch vibration of the carboxylic acid [13] which shifted to band 2586.1 cm-1 after biosorption (Figure 1a). Similar trends were also observed at the absorption band 1832.1 cm-1 and 1163.2 cm-1 (Figure1b) attributed to stretched vibrations of C=O [14] and C-F halides [15] that also shifted to the band 1825.6 cm-1 and 1244.6 cm-1 (Figure.1a), respectively after biosorption process.



**Wavenumber (cm-1)**

**Transmittance (%)**

**Figure 1:** FTIR Spectra of ADFX (a) after biosorption (b) before biosorption

***3.2. Experimental design summary***

The D-optimal design suggested a quadratic model which consists of eighteen experimental runs (18). Run 14 with selected factors; 60 min, 200mg/L and 0.60g which correspond to the tc, *C*o and *B*d, respectively have the highest percentage removal (73.33%) while the highest adsorption capacity of 0.434 mg/g at selected factors of 60 min, 200 mg/L, and 0.20 g was obtained at run 17. However, the lowest percentage removal (4.848 %) and adsorption capacity (0.125 mg/g) were obtained at run 7 and 12, respectively. The results of the diagnostic case studies (Table 3) indicate that the difference between the predicted and actual values for adsorption capacity and percentage removal was small which shows an elevated value of R2 [16]. The results obtained for the normal plot of residuals for both responses (Adsorption capacity and percentage removal) (Figure 2 a-b) show the data points were within a straight line and the level of stacking was less. High R2 was also obtained from the plot of the relationship between the predicted and actual values for both adsorption capacity and percentage removal (Figure 3 a-b).

Table 3: D-optimal design and diagnostic case statistics for the responses

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Run | Factors | | |  | Responses | | | | | | |
| tc (min) | *C*o (mg/L) | *B*d (g) |  | Adsorption Capacity (mg/g) | | |  | percentage removal | | |
|  | Actual Value | Predicted value | Residual |  | Actual Value | Predicted value | Residual |
| 1 | 120 | 150 | 0.4 |  | 0.176 | 0.217 | -0.041 |  | 64.444 | 50.817 | 13.63 |
| 2 | 120 | 50 | 0.2 |  | 0.142 | 0.170 | -0.024 |  | 11.515 | 10.813 | 0.702 |
| 3 | 60 | 150 | 0.6 |  | 0.154 | 0.184 | -0.030 |  | 68.889 | 57.069 | 11.82 |
| 4 | 90 | 150 | 0.2 |  | 0.235 | 0.271 | -0.036 |  | 52.525 | 37.478 | 15.05 |
| 5 | 120 | 50 | 0.2 |  | 0.142 | 0.170 | -0.028 |  | 13.939 | 10.813 | 3.126 |
| 6 | 120 | 200 | 0.6 |  | 0.178 | 0.218 | -0.040 |  | 73.030 | 76.308 | -3.278 |
| 7 | 60 | 50 | 0.2 |  | 0.157 | 0.184 | -0.027 |  | 4.848 | 6.088 | -1.24 |
| 8 | 90 | 100 | 0.5 |  | 0.158 | 0.154 | 0.004 |  | 52.121 | 39.430 | 12.69 |
| 9 | 60 | 50 | 0.2 |  | 0.155 | 0.184 | -0.029 |  | 6.061 | 6.088 | -0.027 |
| 10 | 120 | 200 | 0.2 |  | 0.357 | 0.311 | 0.046 |  | 45.909 | 54.354 | -8.445 |
| 11 | 90 | 50 | 0.4 |  | 0.132 | 0.130 | 0.002 |  | 20.00 | 19.428 | 0.5722 |
| 12 | 120 | 50 | 0.6 |  | 0.125 | 0.077 | 0.048 |  | 24.24 | 32.767 | -8.525 |
| 13 | 60 | 200 | 0.4 |  | 0.284 | 0.278 | 0.006 |  | 56.970 | 60.606 | -3.636 |
| 14 | 60 | 200 | 0.6 |  | 0.176 | 0.231 | -0.055 |  | 73.333 | 71.583 | 1.75 |
| 15 | 120 | 50 | 0.6 |  | 0.126 | 0.077 | 0.049 |  | 23.636 | 32.767 | -9.131 |
| 16 | 120 | 200 | 0.2 |  | 0.316 | 0.311 | 0.005 |  | 52.121 | 54.354 | -2.232 |
| 17 | 60 | 200 | 0.2 |  | 0.434 | 0.325 | 0.109 |  | 34.242 | 49.629 | -15.39 |
| 18 | 60 | 50 | 0.6 |  | 0.131 | 0.090 | 0.041 |  | 20.606 | 28.042 | -7.436 |

|  |  |
| --- | --- |
| (a) | (b) |
| **Figure 2:** Residual Normal plot for (a) adsorption capacity and (b) percentage removal | |

|  |  |
| --- | --- |
| (a) | (b) |
| **Figure 3:** Predicted against actual plot (a) adsorption capacity and (b) percentage removal | |

The R2 obtained for adsorption capacity and percentage removal were 0.8052 and 0.8830 while the corresponding adjusted R2 were 0.7634 and 0.8580. The R2, which should be close to one (1), demonstrates the extent to which response in the model has diminished. A large R2 value implies that the generated model equation reflects the process reasonably and can be used for theoretical model representation [17]:

(7)

(8)

***3.3. Three-dimensional plot of the surface interaction***

From Figure 4a, the adsorption capacity of the ADFX increased when the *C*o increased while the tc reduced. However, the percentage of removal increased when both *C*o and tc increased. Furthermore, the percentage removal increased when the tc and *B*d were increased while the adsorption capacity only increased when the tc was reduced while the *B*d increased (Figure 4b).

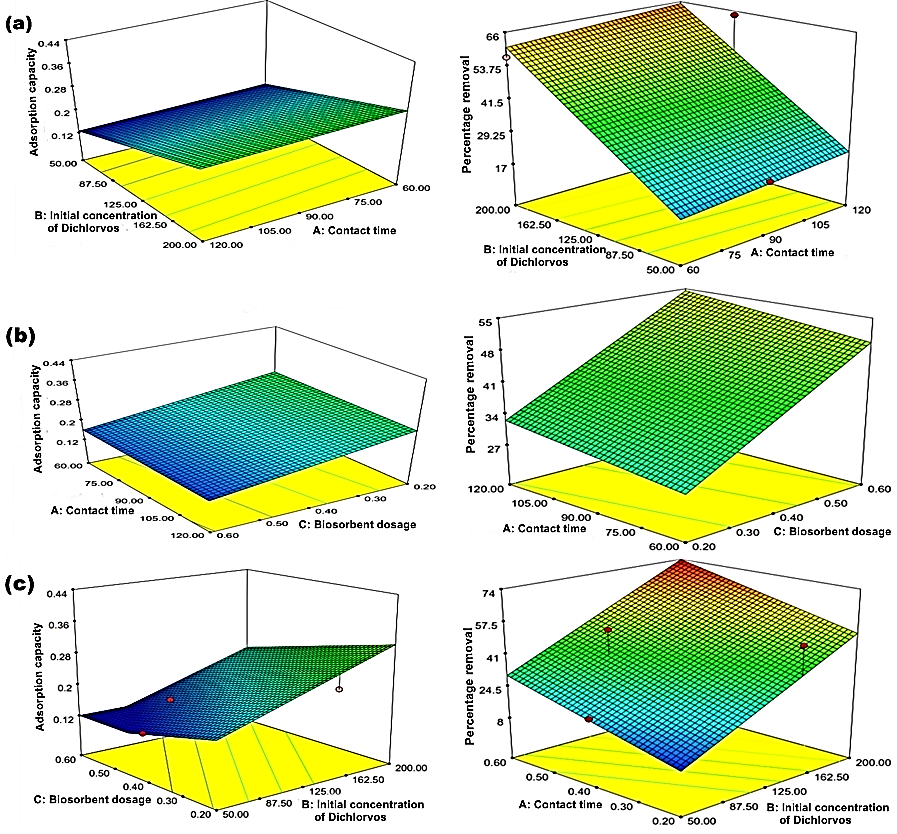


Figure 4: Three-dimensional surface plot revealing the influence of (a) initial concentration of Dichlorvos (Co) and contact time (tc) on adsorption capacity and percentage removal (b) contact time (tc) and biosorbent dosage (*B*d) on adsorption capacity and percentage removal (c) biosorbent dosage (*B*d) and initial concentration of Dichlorvos (Co) on adsorption capacity and percentage removal

The percentage removal also increased when the *Co* and *B*d were increased while the adsorption capacity only increased when the *B*d was lessened while the *C*o also increased (Figure. 4c). The surface of the three-dimensional plots was flat; this implies a direct correlation between the factors selected [18]. This is apparent from the software's regression analytical model (Table 4).

Table 4: Biosorption ANOVA

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Adsorption Capacity | | | | | |
| Source | Sum of Squares | DF | Mean Square | F Value | Prob> F |
| Model | 0.11 | 3 | 0.035 | 15.34 | 0.0001\* |
| A- tc | 6.843E-004 | 1 | 6.843E-004 | 0.30 | 0.5930 |
| B- Co | 0.071 | 1 | 0.071 | 31.12 | < 0.0001\* |
| C- *B*d | 0.031 | 1 | 0.031 | 13.47 | 0.0025\* |
| Residual | 0.032 | 14 | 2.287E-003 |  | NA |
| Lack of Fit | 0.031 | 10 | 3.116E-003 | 14.65 | 0.0099\* |
| Pure Error | 8.510E-004 | 4 | 2.127E-004 | NA | NA |
| Cor Total | 0.14 | 17 | NA | NA | NA |
| **Adequate Precision =** 11.018, **R2** = 0.7668, **Adj. R2** = 0.7168, **Predicted R2** = 0.5807 | | | | | |
| Percentage Removal | | | | | |
| Model | 8308.95 | 3 | 2769.65 | 30.38 | < 0.0001\* |
| A- tc | 82.74 | 1 | 82.74 | 0.91 | 0.3570 |
| B- Co | 6768.10 | 1 | 6768.10 | 74.23 | < 0.0001\* |
| C- *B*d | 1694.31 | 1 | 1694.31 | 18.58 | 0.0007\* |
| Residual | 1276.44 | 14 | 91.17 | NA | NA |
| Lack of Fit | 1253.29 | 10 | 125.33 | 21.65 | 0.0047\* |
| Pure Error | 23.15 | 4 | 5.79 | NA | NA |
| Cor Total | 9585.39 | 17 | 2769.65 | 30.38 | < 0.0001 |
| **Adequate Precision =** 15.600, **R2** = 0.8668, **Adj. R2** = 0.8383, **Predicted R2** = 0.7920 | | | | | |
| NA- Not Applicable \*Significant at P (prob>F) 0.05 | | | | | |

***3.4. Optimization studies***

The model equations (eqn. 8 and 9) representing the objective functions were subjected to the constraint indicated in Table 5. The highest desirability (0.666) was achieved at the maximum adsorption capacity and percentage removal of 0.3113 mg/g and 54.35%, respectively at 120 min tc, 200 mg/L *C*o, and 0.20 g *B*d. The result of the validation at the achieved optimum process condition (Table 6) shows a close relationship between simulated and analytical values of adsorption capacity and percentage removal with a 1.12% and 1.16% error difference. These variations are less than 10% and justify the suitability of the design [19].

***3.5. Effect of contact time (tc) and initial concentration of Dichlorvos (Co)***

The plot of qe against t (Figure 5) shows that the adsorption capacity of the ADFX increased steadily with an increase in both tc and Co. The removal of Dichlorvos was faster in the first 10 min with the uptake of 1.33, 2.08, and 2.75 mg/g at 30, 40, and 50 mg/L Co. The extent of biosorption reduces as the contact time increases steadily until it nearly reached equilibrium when both adsorption and desorption rates tend to be equal [20]. The increase in biosorption was due to the increase in concentration gradient [21] and increased vacant sites on the ADFX [22]. The biosorption process reached equilibrium at 210 min and a maximum adsorption capacity of 1.68, 2.87, and 5.20 mg/g, respectively were achieved. The percentage of removal also increased with increasing tc and Co. The highest percentage removal of 34.16, 43.75, and 64.4% were obtained at 30, 40, and 50 mg/L Co, respectively.

**Table 5:** Subject constraints for the numerical optimization Study

|  |  |  |  |
| --- | --- | --- | --- |
| **Name** | **Goal** | **Lower Limit** | **Upper Limit** |
| tc(min) | is in range | 60 | 120 |
| Co (mg/L) | is in range | 50 | 200 |
| *B*d (g) | is in range | 0.2 | 0.6 |
| Adsorption capacity (mg/g) | Maximize | 0.125 | 0.434 |
| Percentage removal (%) | Maximize | 4.848 | 73.33 |

Table 6: Correlation between the simulated and analytical value

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | tc(min) | Co (mg/L) | *B*d (g) | Adsorption capacity (mg/g) | Percentage removal (%) |
| Analytical | 58.50 | 196 | 0.22 | 0.3278 | 50.50 |
| Simulation | 60.07 | 200 | 0.20 | 0.3382 | 51.04 |

|  |  |
| --- | --- |
|  |  |
| Figure 5: Effect of tc and Co on adsorption capacity and percentage removal (PR) | |

***3.6. Effect of biosorbent dosage (Bd)***

At the different initial concentrations of Dichlorvos (30, 40, and 50 mg/L), the adsorption capacity and percentage removal increased with an increase in *B*d (Figure 6). This was because more adsorption sites on the ADFX became available [23].

***3.7. Effect of temperature***

As presented in Figure 7, the uptake of Dichlorvos by the ADFX rises as the temperature also rises to a certain level. The increase in adsorption capacity and percentage removal with temperature was an indication that the active surface sites on the ADFX have increased with temperature [24]. The extent of biosorption reduces as the contact time increases steadily until it nearly reached equilibrium when the rates of adsorption and desorption tend to be equal. Increasing temperature allows the aggregation process to exceed a certain temperature limit in a specified manner, above which desorption becomes more significant, thereby lessening the biosorption rate as time passes by. The process attains equilibrium at 100 min tc with the highest adsorption capacity of 6.99, 7.30, and 7.40 mg/g at 30, 40, and 50 oC, respectively.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | | |
| Figure 6: Effect of *B*d on adsorption capacity and percentage removal | | | |
|  | |  |
| Figure 7: Effect of temperature on adsorption capacity and percentage removal | | |

***3.8. Analysis of adsorption isotherm***

The model plots for the isotherms are presented in Figure 8 and the calculated parameters are presented in Table 7. The Langmuir isotherm (Figure 8a) suggests monolayer biosorption on the biosorbent surface, with a limited number of uniform adsorption sites. The biosorption involves a comparable mechanism with relations between the adsorbate molecules [25]. The Freundlich isotherm (Figure 8b) is an analytical model that is based on the basic assumption that the biosorption happens on a heterogeneous surface or that the biosorbent affinity differs over the biosorbent surface [26]. The best isotherm model was selected based on the model with the highest R2. Therefore, the Freundlich isotherm with an R2 value of 0.9998, and the best isotherm fitting (Figure 8b) perform better than Langmuir, Dubinin Radushkevich, and Harkins-Jura with corresponding R2 values of 0.8973, 0.9626, and 0.9283.

This is an indication that uptake of Dichlorvos molecules occurs at the heterogeneous surface of the ADFX and the interaction of the Dichlorvos molecules adsorbed follows the Freundlich model [27]. Also, since the ∩ which is Freundlich constant that denotes surface heterogeneity in the adsorption process is less than 1 (0.5841) then it is evident that chemisorption is desirable. Comparisons of the calculated Freundlich parameters with other studies are presented in Table 8.

|  |  |
| --- | --- |
| C:\Users\Raphael\Desktop\cats8.jpg | C:\Users\Raphael\Desktop\cats45.jpg |
| (a) | (b) |
| C:\Users\Raphael\Desktop\cats87.jpg | C:\Users\Raphael\Desktop\cats90.jpg |
| (c) | (d) |
| **Figure 8:** Isotherm plot (a) Langmuir (b) Freundlich (c) Harkin-Jura (d) Dubinin-Radushkevich | |

***3.9. Analysis of kinetics and Diffusion mechanism***

To study the biosorption kinetics, three models were used (PFO, PSO, and Elovich kinetic models). The plots of the models are presented in Figure 9(a-c). The adsorption rate constants, K1 (Table 9)for the PFO were obtained by plotting against t (Figure 9a) while K2 (Table 9) for the PSO was obtained by plotting against t (Figure 9b). Also, the Elovich constant and (Table 9) were obtained from the plot of against (Figure 9c). The value of K1 obtained at 30, 40 and 50 mg/L Co are 0.0028, 0.0046, 0.0062 min-1, respectively. This shows that the rate of adsorption increased with an increase in C*o* while the adsorption capacity at equilibrium decreased. The values obtained for K2 (2.5574, 2.9674, 5.4259 min-1), (1745.7, 373.03, 18.048 mg/gmin2) and (15.221, 4.4683, 1.6111mg/g) show a similar trend.

The criteria for selecting the best kinetics that represents the biosorption of the Dichlorvos onto the ADFX are the coefficient of determination (R2) [28]. The closeness of the R2 value to unity makes the model the best fit. In this study, Elovich with the highest R2 values (0.9730, 0.9454, and 0.8991) at 30, 40, and 50 mg/L Co is the best model that describes the kinetics for the biosorption of Dichlorvos onto ADFX. The possible involvement of particle diffusion during Dichlorvos biosorption was confirmed by greater R2 values obtained for Webber-Morris diffusion (WMD), Dumwald-Wagner diffusion (DWD), and McKay film diffusion (MFD) models plot (Figure 9d-f). The WMD model plot displayed multi-linearity (Figure 9d). The values of , and C (Table 9) were obtained from the slope and intercept of the plots in Figure 9 (d-f). The biosorption mechanism was depicted by the values of C while Kwm, and are the rate factors [29]. A higher value of C indicates better biosorption (Mathangi and Kalavathy, 2018). Since the plot of WMD pass through the origin, then it can be inferred that the process was controlled by particle diffusion while the rate-limiting steps are MFD and DWD [30].

**Table 7:** Parameter of isotherm models for biosorption

|  |  |  |
| --- | --- | --- |
| **Isotherms** | **Parameter** | **ATDX** |
| Langmuir | Qm calculated (mg/g) | -2.6374 |
|  | Ke(mg/g) | -0.0155 |
|  | R2 | 0.8973 |
| Freundlich | Kf (mg/g) | 0.1242 |
|  | 1/n | 1.7119 |
|  | n | 0.5842 |
|  | R2 | 0.9998 |
| Dubinin-Radushkevich | qm (mg/g) | 10.611 |
|  | R2 | 0.9626 |
|  | β | 0.0001 |
|  | ε | 0.1714 |
| Harkins-Jura | A | 0.4155 |
|  | B | 1.5644 |
|  | R2 | 0.9283 |

***3.10. Adsorption thermodynamics***

The plot of lnKd against I/T (Figure 10) was used to determine the thermodynamic properties (Table 10). The positive values of show that the biosorption process was endothermic and therefore, a rise in temperature leads to an increase in the adsorption rate of diffusion of the Dichlorvos through the layer to the internal pore of the biosorbent. Since the value for the obtained at various Co was less than 40 KJ/mol, the mechanism for the biosorption of the Dichlorvos by the biosorbent follows physisorption [34]. The negative values obtained for the change in entropy indicate that the degree of disorderliness during biosorption decreases at the solid-liquid interface [35].

|  |  |  |
| --- | --- | --- |
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | (e) | (f) |
| **Figure 9:** Adsorption kinetics plot (a) PFO (b) PSO (c) Elovich (d) WMD (e) DWD and (f) MFD | | |

**Table 8:** Comparison of Freundlich parameter obtained for Dichlorvos biosorption with other reported adsorbates

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Adsorbate | Biosorbent | Parameter determined | | | Reference |
|  | n |  |  |
| Dichlorvos | ADFX | 0.1241 | 0.5841 | 0.9998 | Present study |
| 2, 4-D | OP | 5.94 | 1.88 | 0.9731 | [31] |
|  | MW | 5.93 | 2.19 | 0.9897 |  |
|  | AS | 7.29 | 3.65 | 0.8954 |  |
|  | BP | 4.72 | 2.22 | 0.9571 |  |
| Oxamyl | SFAC | 27.906 | 1.16 | 0.9975 | [32] |
| Malathion | Phyllantus niruri | 0.6569 | 1.0930 | 0.9987 | [33] |

Table 9: Kinetic and mass transfer diffusion models parameters

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Kinetic model** | | | | | | | | | | | | | | | | | | |
| Co  (mg/L) | (mg/g) | PFO | | | PSO | | | | | | Elovich | | | | | | | |
| (mg/g) |  |  |  | (mg/g) | |  |  | |  | | α | | |  | |  |
| 30 | 1.7083 | 2.5574 | 0.0028 | 0.9633 |  | 1.7083 | | 2.5574 | 0.1427 | |  | | 1745.7 | | | 15.221 | | 0.9730 |
| 40 | 2.9167 | 0.9423 | 0.0046 | 0.9439 |  | 2.9167 | | 2.9674 | 0.0414 | |  | | 373.03 | | | 4.4683 | | 0.9454 |
| 50 | 5.3667 | 0.5514 | 0.0062 | 0.8445 |  | 5.3667 | | 5.4259 | 0.0019 | |  | | 18.048 | | | 1.6111 | | 0.8991 |
| **Diffusion models** | | | | | | | | | | | | | | | | | | |
| Co  (mg/L) | WMD | | | | | | DWD | | | | | | | | MFD | | | |
|  | | |  |  | |  | | |  | |  | |  | | |  | |
| 30 | 0.0163 | | | 1.4574 | 0.9858 | | 0.0196 | | | 0.7704 | |  | | 0.0242 | | | 0.3607 | |
| 40 | 0.0549 | | | 2.0994 | 0.9391 | | 0.0177 | | | 0.7805 | |  | | 0.0225 | | | 0.3873 | |
| 50 | 0.1397 | | | 3.3222 | 0.7520 | | 0.0143 | | | 0.7039 | |  | | 0.0189 | | | 0.1137 | |

PFO: Pseudo First Order, PSO: Pseudo Second Order, WMD: Weber Morris Diffusion, MFD: McKay Film Diffusion and DWD: Dumwald-Wagner Diffusion

**Figure 10**/ plot of InKd vs I/T

Table 10. Thermodynamic parameter for adsorption of DDVP

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Conc  mg/l | Temp  (˚C) | Kd | lnkd | ∆G  (J/mol) | ∆H  (J/mol) | ∆S  (J/mol.K) |  |
| 30 | 30 | 0.04336 | -3.13801 | 7905.08 | 5328.69 | -8.50688 |  |
|  | 40 | 0.04634 | -3.07172 | 7993.48 |  |
|  | 50 | 0.04944 | -3.007 | 8075.07 |  |
| 40 | 30 | 0.07094 | -2.64592 | 6665.44 | 195.92 | -21.3936 |  |
|  | 40 | 0.07003 | -2.6588 | 6918.96 |  |
|  | 50 | 0.07130 | -2.64077 | 7091.59 |  |
| 50 | 30 | 0.07271 | -2.62125 | 6603.31 | 3996.12 | -8.54845 |  |
|  | 40 | 0.07809 | -2.54984 | 6635.40 |  |
|  | 50 | 0.08018 | -2.52348 | 6776.61 |  |

**4. Conclusion**

ADFX biosorbent has been developed and deployed successfully for the biosorption of Dichlorvos from an aqueous solution. The effectiveness of the ADFX has been found to depend greatly on contact time (tc), initial concentration of Dichlorvos (Co), and the dosage of the biosorbent (*B*d). The analytical and simulated data obtained for the biosorption of Dichlorvos shows a close correlation with an error difference of less than 5%. An optimal condition for biosorption based on percentage removal of 52.04% and adsorption capacity of 0.3382 mg/g were 60.07 min tc, 200 mg/L Co and 0.20 g *B*d. The biosorption isotherm and kinetics fitted greatly with the Freundlich isotherm and Elovich models. Also, the diffusion mechanism indicates the film diffusion as the rate-controlling step while the thermodynamics shows that the process was endothermic and the degree of disorderliness decreases at the solid-liquid interface during biosorption. For future studies, the usability of Acid-Activated *Tithonia diversifolia* Xylem for Dichlorvos removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

**Notations and Abbreviations**

|  |  |
| --- | --- |
| : Initial biosorption rate  : Desorption constant.  : Biosorbent dose  : Contact time  : Dumwald-Wagner diffusion rate constant  : Freundlich constant  : McKay film diffusion rate constant  Webber–Morris diffusion rate constant  : Dichlorvos concentration at equilibrium time  : Dichlorvos concentration at initial state (t=0)  (L/min): Pseudo- first-order rate constant  (g/mg.min): Pseudo-second order rate constant  : Equilibrium constant.  : Dubinin–Radushkevich model adsorbate equilibrium concentration  Adsorption capacity at equilibrium  : Maximum monolayer coverage adsorption capacity  : Adsorption capacity at time t  ∆Gº (): Free energy change  ∆Hº (): Change in enthalpy  ∆Sº (): Change in entropy  ∩: Freundlich constant, | 2, 4-D: 2, 4-dichlorophenoxy acetic acid  A: Harkins-Jura constant  AP: Apple shell  B: Harkins-Jura constant  BP: Banana peel  DWD: Dumwald-Wagner Diffusion  KL (L/mg): Biosorption free energy constant  MFD: McKay Film Diffusion  MW: Millet waste  OP: Orange peel  PE (%): Percentage removal  PFO: Pseudo First Order  PSO: Pseudo Second Order  R (: Molar gas constant  R2: Correlation coefficient  SFAC: Silkworm faeces activated carbon  tc (min): Contact time  *T*p (K): Temperature  WMD: Weber Morris Diffusion  : Weber-Morris constant  : Biosorption percentage  : Volume of the synthetic wastewater  Mass of the biosorbent  : Free energy of sorption/mole of adsorbate  : Polanyi potential |

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