Fabrication of Ananas comosus leaf extract modified titanium dioxide nano bio adsorbent for the sequestration of basic dye from aqueous phase: equilibrium and kinetic studies

Nida Fakhar, Weqar Ahmad Siddiqi, Tabrez Alam Khan and Mohammad Fuzail Siddiqui

1 Department of Applied science and Humanities, Faculty of Engineering and Technology, Jamia Millia Islamia, New Delhi, India
2 Department of Chemistry, Jamia Millia Islamia, New Delhi, India

E-mail: wsiddiqui@jmi.ac.in

Keywords: adsorption, water pollution, isotherm, adsorbent

Abstract

A novel, titanium dioxide nano bio-adsorbent (TiO$_2$L) based on Ananas comosus leaf extract was developed by sol-gel route and was subsequently used to decolorize toxic non-biodegradable basic dye Victoria blue (VB) from the aqueous solution. Several techniques were used to characterize the synthesized bio-adsorbent like XRD, FTIR, SEM-EDX and TEM to observe physio-chemical changes and adsorption interactions. The impact of process parameters on the adsorption behavior of TiO$_2$L towards VB were comprehensively studied and the optimized conditions were initial dye concentration (50 mg L$^{-1}$), dose (1.8 g L$^{-1}$), contact time (40 min), and pH (6) of the solution. Different isotherm and kinetic models were used to analyze the equilibrium data among which Langmuir model appropriately fitted the equilibrium data based on high R$^2$ (0.994) and pseudo second order described the reaction kinetics of VB adsorption onto the adsorbent. The maximum adsorption capacity was found to be 83 mg g$^{-1}$. Dye loaded adsorbent was regenerated and used for 3 cycles without subsequent loss in its efficiency. Thus, economic feasibility, environmentally friendly, better sorption capacity and regeneration potential, validates TiO$_2$L as a potential adsorbent for VB from wastewater.

1. Introduction

Since 21th century, many countries have accounted the efficient use of energy resources but an ever-escalating environmental pollution is still an issue that have not been completely resolved. One such problem is of dye wastewater that have hazardous impact on the environment [1]. Although current utilization of 5Rs of waste management that are refuse, reuse, reduce, recovery and recycle, there is unstoppable multiplication in sizes and the numbers of waste disposal sites which is associated with fast industrialization, urbanization, human migration from village to cities and other anthropogenic activities [2]. Presently, about fourteen million chemicals above threshold level are toxic that are found in environment [3]. Dyes are notorious pollutant among the chemicals found in textile wastewater that are responsible for severe health and environmental issues [4]. Liberation of effluents by industries over past few years have elevated environmental pollution significantly. These discharged pollutants alter the condition of environment and poses serious environmental problems [5]. Being used as a shading factor in distinct industries like cosmetics, textiles, printing, food, dye synthesis, and plastics, dyes are not only toxic to human race but also ruinous to aquatic life [6]. The dye-laden wastewater released not only alters aesthetic nature but also cutback the light transmittance in water thus declining the photosynthetic activity. Further, they are carcinogenic, mutagenic, and teratogenic to the biotic life [7]. Therefore, their sequestration from wastewater has been greatly acknowledged over past few years. Victoria blue (VB) a cationic dye, due to its photosensitizing effect generates cytotoxic response in mammalian cell lines which in turn promote toxicity [8]. It further has detrimental consequences on living beings, thus requires a proper remediation from the aquatic environment by a method which is economically feasible and environmentally...
All the reagents were of analytical grade. Titanium iso-propoxide was added and stirred for next 30 min and the solution was stirred for 30 min. 50 ml of Titanium iso-propoxide was added and stirred for next 30 min [25]. In the stirring obtained suspension, leaves extract supernatant was also added. Then the suspension was kept in water bath approximately for 1 h at 95 °C, filtered and separated and kept at 80 °C for complete drying and stored in glass bottle.

2. Materials and Instrumentation

All the reagents were of analytical grade. Titanium iso-propoxide (Merck, India) (C₁₂H₂₈O₄Ti), Victoria blue (CAS no 2580-56-5) (Himedia), Urea (CO(NH₂)₂) (Merck, India). X-ray diffractometer(XRD) analysis were obtained using Regaker ultimar IV X-ray diffractrometer (Japan), Fourier transform infra-red spectroscopy (FTIR) spectra were recorded in the range of (400–4000 cm⁻¹) on Perkin Elmer 580B spectrophotometer, Scanning electron microscopy/Energy dispersive X-ray(SEM/EDX) micrographs were obtained on JEOL-6510LV (Germany) and Transmission electron microscopy(TEM) images were taken on JEOL-EM410LS.

2.1. Preparation of TiO₂L Nano bio-adsorbent

100 g of dried pineapple fiber leaves (Ananas comosus) was grinded. The obtained material was refluxed at 70 °C with distilled water for 2 h and cooled at 25 °C for 1 h. The aqueous extract of Ananas comosus leaves was centrifuged and supernatant was collected by filtration. For the preparation of nano bio adsorbent, dispersion of 1 g urea in 200 ml Double distilled water (DDW) and the solution was stirred for 30 min. 50 ml of Titanium iso-propoxide was added and stirred for next 30 min [25]. In the stirring obtained suspension, leaves extract supernatant was also added. Then the suspension was kept in water bath approximately for 1 h at 95 °C, filtered and separated and kept at 80 °C for complete drying and stored in glass bottle.
2.2. Adsorption investigation

The adsorption process was investigated by batch mode and effect of parameters such as adsorbent dose, contact time, adsorbate concentration, and initial pH were examined. For this fixed amount of TiO$_2$L adsorbent ($1.2–2.4$ g L$^{-1}$) was added to the $25$ mL solution of Victoria blue dye of different concentration ($30–80$ mg L$^{-1}$) for the $40$ min contact time. The effect of pH on the adsorption of Victoria blue was investigated by varying the solution pH from $2$ to $10$ and keeping all other parameter constant. Further the solution was centrifuged for $5$ min at $1000$ rpm and the supernatant remaining concentration was determined by UV–vis spectrophotometer at $610$ nm. The values of adsorption capacity at equilibrium (equation (2)) and % Removal efficiency were calculated by equation (1)

\[
\text{% Removal efficiency} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

where $C_0$ and $C_e$ are initial dye concentration and dye concentration at equilibrium.

The Victoria blue dye amount adsorbed on the *Ananas comosus* leaves extract modified TiO$_2$L nano bio-adsorbent was estimated from equations (2) and (3)

\[
Q_e = \left[\frac{C_0 - C_e}{V}\right] \times \frac{W}{W}
\]

\[
Q_t = \left[\frac{C_0 - C_t}{V}\right] \times \frac{W}{W}
\]

where, $Q_e$ and $Q_t$ are the adsorption capacity at equilibrium and time $t$. $C_t$ is the concentration at equilibrium.

3. Results and discussions

3.1. Characterization of TiO$_2$L nano bio adsorbent

The XRD analysis (figure 1) of pure TiO$_2$ demonstrated crystalline nature due to the presence of several sharp peaks with h k l values at $25.26^\circ$ (101), $37.96^\circ$ (112), $48.13^\circ$ (200), $54.90^\circ$ (211), $63.59^\circ$ (204) and $75.88^\circ$ (215). The XRD diagram was well matched with database of ICPDS No. 21–1272. The main 2θ peak detected at $25.32$ referred to 101 is anatase value. It was observed that the anatase peak demonstrated a shift to $25.93^\circ$ with a reduction in intensity corroborates the formation of the bio-adsorbent. Further, a shift in almost every peak in TiO$_2$L ($38.09^\circ$, $47.60^\circ$, $54.04^\circ$, $55.94^\circ$, $62.38^\circ$, $75.48^\circ$) and an appearance of a little hump demonstrated decline in crystallinity in the synthesized bio-adsorbent which validates the formation TiO$_2$L bio-adsorbent. The calculated crystallite size using Scherer’s equation was $25$ nm which is in good agreement with TEM studies. FTIR analysis (figure 2) of Pure TiO$_2$ shows corresponding peaks at $3346$ cm$^{-1}$, $1640$ cm$^{-1}$ which are assigned to –OH stretching and bending vibrations respectively [26]. The broad absorption peak at $500–700$cm$^{-1}$
corresponds to Ti-O stretching and Ti–O–Ti bridging stretching modes [27] which demonstrate anatase phase of Titania. In the TiO2L same bands were observed as in pure TiO2 but with considerable shifts. The –OH stretching and bending peaks were shifted to 3180 cm–1 and 1552 cm–1 with an increase in broadness which confirms the formation of bio-adsorbent [28]. In FTIR analysis of dye loaded TiO2L the decrease in the intensity of –OH peak at 1552 cm–1 clearly governs the occurrence of hydrogen bonding which might be responsible for the uptake of dye on the synthesized bio-adsorbent.

The analysis of SEM was undertaken to acknowledge the pattern and know the morphology of TiO2L and after the adsorption of the dye shown in figures 3(a) and (b). The surface texture shows irregular surface which is porous having cavities indicating the accommodation of adsorbate captured and adsorbed on the surface. The SEM image shows filled pores and cavities with more regular surface indicating the adsorption of adsorbate on the surface after adsorption. EDX after adsorption displayed an intense carbon peak which confirmed the sorption of VB on TiO2L. The transmission electron microscopy clearly reveals the spherical shaped morphology of TiO2L as shown in figure 4(a) The images confirmed that Nano spheroids are formed and agglomerated with average crystallite size as observed through particle size distribution curve is 5.5 nm as shown in figure 4(b)

3.2. Effect of process parameters on adsorption of VB dye

3.2.1. Effect of sorbent dose

The effect of sorbent dose on % removal is depicted in figure 5(a), with respect to the varied sorbent dose from (1.2, 1.4, 1.6, 1.8, 2, 2.2 and 2.4 g L–1). An escalation in the % removal was observed on increasing the adsorbent dose. The maximum uptake of VB (94.03%) was noticed at the adsorbent dose of 1.8g L–1 which might be attributed to an increase in number of binding sites. Elevated dose from 2g L–1 resulted in unaltered adsorption phenomenon because of over indulging of adsorbent that ultimately leads to no further increase in surface area which limits the adsorption phenomenon [29]. Adsorbent dosage of 1.8g L–1 was taken for further experiments.

3.2.2. Effect of contact time

The contact time influence on the sequestration of VB was studied in the range of 10–60 min at room temperature. An increase in contact time revealed the amount of dye adsorbed increases and reached an equilibrium state at 40 min as shown in figure 5(b), which is due to the large availability of active sites. As the time period was increased further negligible effect on adsorption rate was observed which might be due to the unavailability of binding sites. Therefore, a time period of 40 min was taken for further study.
3.2.3. Effect of initial dye concentration
Adsorption of VB dye was studied at different initial concentration 30–80 mg L\(^{-1}\) at 25 °C keeping other parameters, dose (1.8 g L\(^{-1}\)), contact time (40 min) and pH (7) constant. Figure 5(c) indicates that maximum removal was achieved at 50 mg L\(^{-1}\) and with further increase in initial dye concentration a decrease was observed. This trend can be due to the availability of sites initially which get filled at higher concentration that abates the removal percentage.

3.2.4. Effect of pH
The influence of pH parameter is important in the process of adsorption. The increase in curve was noticed with increase in pH (2–10) until it reached to the stability state. The maximum adsorption of VB dye occurred on initial pH 6. Further, increase in pH from 8 to 10 it was seen that the adsorption capacity does not increases so effectively as shown in figure 5(d). Surface functionality of adsorbent and sorbate are responsible for the pH effect to be dominant. In the acidic medium there is decrease in adsorption of VB because H\(^+\) ions in acidic medium competes with the VB dye for the free active sites [30].

3.3. Adsorption isotherm studies
The fundamental tool to elucidate the nature of adsorbent surface is Adsorption Isotherm. It is significant in describing the adsorbate molecule distribution between the solid and liquid phase at equilibrium. Also, the information about the optimum use of adsorbent is provided by adsorption isotherms. Certain adsorption models such as Langmuir, Freundlich, Temkin and Dubinnin-Radushkevich Isotherm were employed to illustrate the adsorption system. The applicability of different isotherm models was based on the correlation coefficient (R\(^2\)).

3.3.1. Langmuir isotherm
Langmuir isotherm thrusts homogenous sorption of sorbate on the sorbent. This is characterized by monolayer adsorption [31]. The linearized equation of the model is presented by equation (4) [32].

\[
\frac{C_e}{Q_e} = \frac{1}{Q_0b} + \frac{C_e}{Q_0}
\]  
(4)

Where, \(C_e\) is remaining concentration of Victoria blue, \(Q_e\) is adsorption capacity at equilibrium, and \(Q_0\) (mg g\(^{-1}\)) and \(b\) (L mg\(^{-1}\)) are Langmuir constant linked to maximum adsorption capacity and energy of
adsorption. The plot $C_e/Q_e$ Versus $C_e$ that is linear theorize the suitability of this model to this work, exhibiting the formation of monolayer on the adsorbent as shown in figure 6. The slope and intercept of plot gives the value of $Q_0$ and $b$ respectively. The important feature of Langmuir isotherm can be represented by separation factor $R_L$ that is dimensionless constant for equilibrium parameter given by equation (5)

$$R_L = \frac{1}{1 + bC_i}$$

Where $C_i$ is initial concentration, the value of $R_L$ signifies the nature of adsorption to be either favorable if $0 < R_L < 1$, linear if $R_L = 1$, unfavorable if $R_L > 1$ and irreversible if $R_L = 0$. From this investigation the value of $R_L$ (0.066–0.110) was found to be favorable as it is greater than 0 but less than unity suggesting Langmuir model to be appropriate. In this work, the determined maximum monolayer coverage capacity $Q_0$ is 83.3 mg g$^{-1}$ and $b$ values are (0.280–0.160 L mg$^{-1}$) indicating favorable equilibrium sorption. Further the correlation coefficient $R^2$ was 0.994 that govern the suitability of this model.

### 3.3.2. Freundlich isotherm

This isotherm is empirical model employed for adsorbent nature that is heterogenous. This is characterized multilayer adsorption $[31]$. The linear form of this isotherm was tested against dye adsorption was given by equation (6) $[33]$.

---

**Figure 4.** TEM image (a) of TiO$_2$L nano bio adsorbent, (b) particle size distribution curve of TiO$_2$L nano bio adsorbent.
\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  

(6)

\( K_f (\text{L g}^{-1}) \) is the Freundlich isotherm constant which is approximate adsorption capacity indicator in the adsorption process, \(1/ n \) defines adsorption strength in the adsorption process [34]. If \( n = 1 \) then the partition between the two phases are independent of the concentration. If \( 1/ n \) value is less than 1 it signifies normal adsorption whereas if \( 1/ n \) is greater than unity than it shows cooperative adsorption [35] and their values were estimated from the plot of \( \log Q_e \log C_e \) (figure 7) which are presented in table 1. Specifically, equations
that are linearly transformed generally applied to associate sorption data in which $1/n$ is the heterogeneity parameter where the smaller $1/n$, greater the heterogeneity expected [36]. The calculated values of $1/n$ were found to be (0.60–0.66) which suggested favorable and normal sorption process. The regression coefficient $R^2$ (0.987, 0.970, 0.985) at three test temperatures (298, 303, 313 K) revealed that experimental data have very good compatibility with the model but is lesser than Langmuir model.

### Table 1. Isotherms parameter at different temperatures.

| Isotherms     | Parameters | 298 K   | 303 K   | 313 K   |
|---------------|------------|---------|---------|---------|
| Langmuir      | b (L mg$^{-1}$) | 0.160   | 0.189   | 0.280   |
|               | $Q_0$ (mg g$^{-1}$) | 83.3    | 79.3    | 71.4    |
|               | $R^2$      | 0.937   | 0.956   | 0.994   |
|               | $R_L$      | 0.11    | 0.095   | 0.066   |
| Freundlich    | $K_F$ (L g$^{-1}$) | 12.6    | 13.4    | 16.2    |
|               | $1/n$      | 0.66    | 0.65    | 0.60    |
|               | $R^2$      | 0.987   | 0.970   | 0.985   |
| Temkin        | $A_T$ (L mg$^{-1}$) | 1.5     | 1.7     | 2.4     |
|               | $b_T$ (J mol$^{-1}$) | 17.70   | 17.62   | 16.42   |
|               | $R^2$      | 0.977   | 0.977   | 0.99    |
| D-R           | $Q_D$ (mg g$^{-1}$) | 3.67    | 3.711   | 3.698   |
|               | $R^2$      | 0.914   | 0.957   | 0.950   |
|               | $E$ (kJ mol$^{-1}$) | 1.2     | 1.0     | 0.91    |

3.3.3. **Temkin isotherm**

This isotherm has parameter explaining the link between the adsorbent and adsorbing species [37]. As indicated from equation, its derivation described by binding energies having uniform distribution was executed by plotting the sorbed quantity $Q_e$ versus $\ln C_e$. The slope and intercept give Temkin constant. The linear form of isotherm is given by equation (7) [38].

$$Q_e = \left[\frac{RT}{b_T}\right] \ln A_T + \left[\frac{RT}{b_T}\right] \ln C_e$$  \hspace{1cm} (7)

Where, $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $b_T$ (J mol$^{-1}$) constant related to heat of adsorption. $T$ is temperature(K) and $A_T$ (L/g) are equilibrium binding constant linked to binding energy that is maximum between adsorbent and adsorbate (figure 8). From the Temkin plot values of $A_T$ are 1.5, 1.7, 2.4 L g$^{-1}$ at 298, 303, 313 K.

![Figure 7. Freundlich Adsorption Isotherm at temperature 298, 303 and 313 K.](image_url)
313 K which indicates increase in binding energy with rise in temperature. The values of $b_T$ was found to be 0.0177, 0.0176, 0.164 (J mol$^{-1}$) at 298, 303, 313 K suggesting a small change in heat of adsorption with an increase in temperature. The coefficient of regression $R^2$ (0.97, 0.97, 0.99) at three test temperatures (298, 303, 313 K) recommend that adsorption data fitted well to Temkin isotherm.

3.3.4. Dubinin-Radushkevich isotherm

This model is also an empirical model that defines that adsorption occurs at both homogenous and heterogenous surfaces [39]. D-R isotherm denoted linearly by equation (8)

$$\ln Q_e = \ln Q_D - \beta \varepsilon^2$$

where, the saturation capacity of adsorbent is $Q_D$ (mg g$^{-1}$), a constant linked to mean free energy of adsorption per mole of adsorbate is $\beta$ (mol$^2$ J$^{-2}$), a logarithm function of concentration of Victoria blue called Polanyi potential given by equation (9)

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$

$\beta$ and the $Q_D$ values are obtained by slope of plot between $\ln Q_e$ and $\varepsilon^2$ (figure 9). The uniqueness of this isotherm is that it is temperature-dependent in which when data of adsorption at different temperature is plotted as function of logarithm of adsorbed amount $\ln Q_e$ versus $\varepsilon^2$, all data will lie on the same characteristic curve [40]. From the D–R plot values of $Q_D$ are tabulated in table 1 at temperature 298, 303 313 K are 3.67, 3.71, 3.69 mg g$^{-1}$ respectively and are almost constant. The Energy of adsorption, $E$ values were estimated to be (1.2, 1, 0.91 kJ mol$^{-1}$) at different temperature is <8 kJ mol$^{-1}$ which indicated the adsorption of VB on TiO$_2$L might be a physical process [41]. The regression coefficient values, $R^2$ (0.91, 0.95, 0.95) specifies that experimental data showed least fit when compared to other isotherm models. Further, the positive $E$ values shows the endothermic process and process of adsorption favored at lower temperature.

3.4. Kinetics of adsorption

To investigate the adsorption efficiency and mechanism of the system, two kinetic models (Pseudo-first order and pseudo-second order were incorporated to examine the experimental data achieved by altering the contact time [31]. The establishment of kinetic model of Pseudo-first order is on the theory of membrane diffusion and Pseudo-second order based on rate limiting step of adsorption along with mechanism of adsorption [42].
3.4.1. Pseudo-first order model
Lagerngren proposed the adsorption rate constant and Ho by employing first-order kinetic reaction denoted by linear equation equation (10)

\[
\log(Q_e - Q_t) = \log Q_e - k_1 \times \frac{t}{2.303}
\]

where, the first order adsorption rate constant is \(k_1 (\text{min}^{-1})\), the amount of adsorbate adsorbed at time \(t\) is \(Q_t (\text{mg g}^{-1})\) and the amount of adsorbate adsorbed at equilibrium is \(Q_e (\text{mg g}^{-1})\). \(k_1\) is achieved from the straight-line plot of \(\log(Q_e - Q_t)\) versus \(t\) (figure 10). Pseudo-first order rate constant found to be 0.038 min\(^{-1}\). The coefficient of regression \((R^2)\) is 0.85 for the plot, which is not close to unity indicating adsorption data not fitted well to Pseudo-first order kinetics of sorption of VB onto TiO\(_2\)l.

3.4.2. Pseudo second order model
This kinetic model explains the formation of bond between the adsorbent and adsorbate as rate-limiting step by chemisorption. This kinetic model is linearly given by equation (11)

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
\]

Where, overall rate constant for second order adsorption is \(k_2 (\text{mg g}^{-1}\text{ min}^{-1})\). The kinetic plot of \(t/Q_t\) versus \(t\) for Victoria blue adsorption is shown in (figure 11) and various parameters are given in table 2. The coefficient of regression \((R^2)\) is 1, indicates that adsorption data is very well fitted to pseudo-second order kinetics. The value of \(Q_e\) calculated from plot comes out to be 86 mg g\(^{-1}\).

3.4.3. Diffusion models
Adsorption kinetics generally investigate the steps that affect the adsorption process (a) Film diffusion i.e. mass diffusion from bulk solution of adsorbate to the absorbent’s exterior surface (b) Intra particle diffusion i.e. Adsorbate diffusion from exterior surface to adsorbent inner pores and (c) covering of adsorbent active inner and outer sites by adsorbate. Generally, mechanism is controlled by either or both (a) and (b) simultaneously.

The experimental data was fitted to Weber-Morris equation [43] that is expressed as equation (12)

\[
Q_t = K_i t^{0.5} + C_i
\]

while, \(Q_t\) is adsorption capacity, \(K_i\) is constant of intra-particle diffusion rate and \(C_i\) is the intercept. The \(K_i\) (0.393 mg/g/min\(^{0.5}\)) and \(C_i\) (29.98) values can be obtained from slope and intercept of linear plot of \(Q_t\) versus \(t^{0.5}\) (figure 12). The parameter values along with \(R^2\) are tabulated in table 2. According to equation (12), if intraparticle diffusion is influencing the kinetics of adsorption, the result of the plot between \(Q_t\) and \(t^{0.5}\) yields the

![Figure 9. D-R Adsorption Isotherm at temperature 298, 303 and 313 K.](image)
straight line passing through the origin. The plot illustrated three regions that are linear, initial one intended to cover the exterior of adsorbent surface by the adsorbate molecules. There was gradual adsorption akin to intra-particle diffusion of adsorbate by the adsorbent’s pores in second region. The third region depicted the slowdown i.e. equilibrium stage owing to lack of adequate amount of adsorbate molecules and adsorption sites [44]. It is depicted from figure 12 that plot did not pass through the origin that implies mechanism of intra particle was not only rate controlling adsorption kinetics. The higher value of $C_i$ ($29.98$) indicates greater external surface effects the mechanism of adsorption [45].

The adsorption kinetics was then checked using Boyd model of kinetics [46] that is expressed as equation (13)
| Pseudo-first order | Pseudo-second order | Film diffusion model | Intraparticle diffusion model |
|--------------------|---------------------|----------------------|-------------------------------|
| \( k_1 (\text{min}^{-1}) \) | \( Q_e (\text{mg/g}) \) | \( R^2 \) | \( k_f (\text{g/mg/min}^{-1}) \) | \( 0.4 \times 10^{-3} \) | \( Q_e (\text{mg/g}) \) | \( R^2 \) | \( K_d (1/\text{min}) \) | Intercept | \( R^2 \) | \( K (\text{mg/g/min}^{0.5}) \) | Intercept | \( R^2 \) |
| 0.038 | 60.21 | 0.85 | 86.95 | 1 | 0.101 | 1.83 | 0.85 | 0.393 | 29.98 | 0.77 |

Table 2. Kinetics parameters.
While, $K_D \text{ (1 min}^{-1})$ denotes liquid film diffusion constant and $F = Q_t/Q_e$ that is the fractional attainment of equilibrium at time t, as noticeable from (figure 13) plot $-\ln (1-F)$ versus t is linear but did not pass through origin which predicted that the external mass transfer mechanism controlled the rate limiting step in mechanism of adsorption [47].

$$-\ln (1-F) = K_D t \quad (13)$$
4. Desorption and reusability

The economic feasibility of the TiO2L is thought to have important effect on adsorption process. For this case, the adsorbent reusability was tested through three adsorption-desorption cycles [48]. The quantity of adsorbent used in each cycle is 100 mg per 50 ml of 50 ppm agitated for 40 min. Efficiencies of Desorption was estimated by equation (14).

\[
\text{Desorption} \, (\%) = \frac{C_d V_d}{(C_o - C_d) \cdot V_a} \times 100 \tag{14}
\]

In this equation, \(C_d\) and \(V_d\) are concentration at equilibrium and volume of desorption solution, \(C_o\) and \(C_d\) are initial and equilibrium concentration of adsorption respectively. \(V_a\) is volume of adsorption solution. Victoria blue adsorption takes place using fresh adsorbent was 95.7% in first cycle, 91.55% and 88.25% in second and third cycle. Almost 91.4% desorption acquired in first cycle 90.22% in second round and 84.81% in third cycle. The relatively high performance of adsorption-desorption experiment exhibit that adsorbent could be used and regenerated. The regeneration capability suggests good reusability and implies that TiO2L nano bio adsorbent could separate Victoria blue dye from water and wastewater with good feasibleness.

5. Conclusion

In this work, we synthesized a novel green assisted titanium oxide nano bio-adsorbent (TiO2L) from Ananas comosus leaves extract and probed it as an adsorbent for Victoria blue (a cationic dye). The influence of operative variables like dosage (1.8g L\(^{-1}\)), contact time (40 min), pH (6) and initial dye concentration (50 mg L\(^{-1}\)) were thoroughly studied. A sequestration of more than 95% Victoria blue dye was observed within the first 30 min of process corresponding to high adsorption kinetic values. Different isotherm models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm) were utilized to analyze the equilibrium data among which Langmuir model exhibited a best fit with a correlation coefficient of \(R^2 = 0.994\) and maximum adsorption capacity of 83 mg g\(^{-1}\) which was better than most of the reported adsorbents. Pseudo-second order model appropriate the kinetic studies based on correlation coefficient \(R^2 = 1\) among the various models used. It was concluded that TiO2L is cost-effective, non-toxic and exhibited a better adsorption capacity along with a good regeneration potential up to 3 cycles which authenticates it as a promising low-cost adsorbent for Victoria blue.

ORCID iDs

Weqar Ahmad Siddiqi  https://orcid.org/0000-0002-9044-3395

References

[1] Jiang C, Wang X, Qin D, Da W, Hao C and Wu J 2019 J. Hazard. Mater. 369 50–61
[2] Jbab M, Abbas M, Nisar J, Nazir A and Qamar A 2019 Chem. Int. 5 1–80
[3] Jbab M 2016 Chemosphere 144 785–802
[4] Diehaf K, Bouyakoub A Z, Ouhib R, Benmansour H, Mahdad A, Moulay N, Bensaid D and Ameri M 2017 Chem. Int. 3 314–8
[5] Khan S A, Siddiqui M F and Khan T A 2020 Ultrasound.—Sonochem. 69 104761
[6] Ahmed M J K, Ahmaruzzaman M and Borello M H 2015 RSC Adv. 5 74645–55
[7] Wang X, Jiang C, Hou B, Wang Y, Hao C and Wu J 2018 Chemosphere. 206 587–96
[8] Kumar M and Tamilarasam R 2013 J. Chem. Eng. Data 58 517–27
[9] Nazar N, Bibi I, Kamal S, Jbab M, Nouren S, Ilkani K, Umair M and Ata S 2018 Int. J. Biol. Macromol. 106 1203–10
[10] Mahapatra A, Mishra B G and Hota G 2013 J. Hazard. Mater. 258–259 116–23
[11] Siddiqui M F, Khan F and Alarn Khan T 2019 Environ. Prog. Sustain. Energy 38 6
[12] Bhatia D, Datta D, Joshi A, Gupta S and Gote Y 2018 J. Chem. Eng. Data 63 436–45
[13] Djilani C, Zaghoudi R, Dyazi F, Bouschekima B, Lallam A, Modarresi A and Rogalaki M 2015 J. Taiwan Inst. Chem. Eng. 53 112–21
[14] Bibi I et al 2017 Int J Biol. Macromol. 103 783–90
[15] Bibi I et al 2017 Adv. Powder. Technol. 28 2035–43
[16] Cherian B M, Leão A L, De Souza S F, Costa L M M, De Olyveira G M, Kottaisamy M, Nagarajan E R and Thomas S 2011 Carbohydr. Polym. 86 1790–8
[17] Hazarika D, Gogoi N, Jose S, Das R and Basu G 2017 J. Clean. Prod. 141 580–6
[18] Tanpichai S, Wityayakran S and Boonmahitthisut A 2019 J. Environ. Chem. Eng. 7 102836
[19] Remya V R, Abitha V K, Rajput P S, Rame A V and Dutta A 2017 Chem. Int. 3 165–71
[20] Igwe O U and NWanmezie F 2018 Chem. Int. 4 60–6
[21] Pourreza N, Rastegarzadeh S and Larki A 2014 J. Ind. Eng. Chem. 20 2680–6
[22] Ganesan S, Babu I G, Mahendran D, Arulselvi P L, Elango V N, Geetha N and Venkatachalam P 2016 Ann. Phytomedicine An Int. J. 5 69–75
[23] Ng H K M and Leo C P 2019 Col Surf. A Physicochem. Eng. Asp. 578 123590
[24] Zhou J, Hao B, Wang L, Ma J and Cheng W 2017 Sep. Purif. Technol. 176 193–9
[25] Gupta S M and Tripathi M 2012 Cent. Eur. J. Chem. 10 279–94
[26] Manassah J 2011 Proc. of the Int. Conf. on Green Technology and Environmental Conservation GTEC 356–61
[27] Yu J, Su Y, Cheng B and Zhou M 2006 J. Mol. Catal. A Chem. 258 104–12
[28] Khakpash N, Simchi A and Jafari T 2012 J. Mater. Sci.: Mater. Electron 23 659–67
[29] Tripathi A and Narayanan S 2018 Environ. Nanotechnology, Monit. Manag. 10 280–91
[30] Leung W H, Lo W H and Chan P H 2015 RSC Adv. 5 90022–30
[31] Wang X, Wang Y, Hou H, Wang J and Hao C 2017 ACS Sustainable Chem. Eng. 5 6438–46
[32] Langmuir I 1918 J. Am. Chem. Soc. 40 1361–403
[33] Freundlich H M F 1906 Adsorption in solution Z. Phys. Chem. 57 385–470
[34] Voudrias E, Fytianos F and Bozani E 2002 Global Nest the Int. J. 4 175–83
[35] Mohan S and Karthikeyan I 1997 Environ. Pollut. 97 183–7
[36] Goldberg S 2005 Chemical Processes in Soils. SSSA Book Series 8 677
[37] Schulthess C P and Sparks D L 1991 Adv. soil Sci Springer, Berlin, Germany 121–63
[38] Tempkin M I and Pyzhev V 1940 Acta Phys. Chim. USSR 12 327–56
[39] Dubinin M M and Radushkevich L V 1947 Proc. Acad. Sci. Phys. Chem. Sect. 55 331
[40] Foo K Y and Hameed B H V 2010 Chem. Eng. J 156 2–10
[41] Unlu N and Erosat M 2006 J. Hazard. Mater. B 136 272–80
[42] Jiang C, Wang X, Wang G, Hao C, Li X and Li T 2019 Compos. Part B. Eng. 169 45–54
[43] Weber W J and Morris J C 1963 J. Sanit. Eng. Div. 89 31–60
[44] Wang X, Pan J, Guan W, Dai J, Zou X, Yan Y, Li C and Hu W 2011 J. Chem. Eng. Data. 56 2793–801
[45] Khan T A, Dahiya S and Khan E A 2017 Environ Prog Sustain Energy 36 45–58
[46] Boyd G E, Adamson A W and Myers L S 1947 J. Am. Chem. Soc. 69 2836–3284
[47] Radi S, Tighadouini S, Massaoudi M E L, Bacquet M, Degouini S, Revel B and Mahkhot Y N 2015 J. Chem. Eng. Data. 60 2915–25
[48] Shao L, Chang X, Zhang Y, Huang Y, Yao Y and Guo Z 2015 Appl. Surf. Sci. 280 989–92