

Adsorption Characteristics, Diffusion and Isotherms of Modified Pig Waste for Removing Reactive Violet 5

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Abstract:- The present study investigated the adsorption characteristics, diffusion, and Isotherms of modified pig Waste for removing Reactive Violet 5 (RV5). Pig wastes were subjected to chemical modification by Triton X100 (TX100) and 1% sodium dodecyl sulphate (SDS) treatment. The effect of some significant parameters such as pH, time, and dye concentration on the adsorption capacity of the studied systems was determined using standard methods. The pseudo-second-order, intra-particle diffusion, Elovich, and power function kinetic equation models were used to examine the rate of the adsorption process; while the equilibrium data were fitted to adsorption isotherm models; Langmuir, Freundlich, Redlich-Peterson, and Sips models. The maximum RV5 removal capacity for each of the adsorbents was found to be at pH 1 and decreased with increasing pH, and equilibrium time was found to be 80mins for different adsorbent materials, and the adsorption capacity at the equilibrium time was 45%, 48%, and 70% for untreated, TX100 and SDS treated PGD. The results obtained closely fitted into the intraparticle diffusion linear kinetic model with a non-zero y-axis intercept and correlation coefficients (R^2) values of 0.999 for the adsorbents; indicative of a multi-path diffusion mechanism being involved in the adsorption of RV5 by treated and untreated PGD. The adsorption of RV5 by PGD treated with SDS and TX100 strongly aligned with a linearized Freundlich Isotherm for the effect of dye concentration on adsorption capacity; with correlation coefficient (R^2) of 0.968 and 0.937 for the PGD treated with SDS and TX100 respectively. Therefore, PGD treated with SDS may be efficiently used as an adsorbent for the removal of RV5 from aqueous solutions. The adsorption of SDS and TX100 treated PGD tightly fitted into pseudo-second-order, power function, and Elovich non-linear kinetic models and a heterogeneous multi-path diffusion mechanism.

Keywords: Reactive Violet 5, Agricultural waste, modified pig waste, Adsorption isotherms and kinetics.

I. INTRODUCTION

Industrialization has made a deep impact on human health directly or indirectly creating environmental (air, water, soil) pollution by releasing wastes and untreated wastewater into the environment. As a result of increased industrialization, there has been a rise in the discharge of toxic chemicals like azo-dyes into the environment. Dyes are extensively used in the industries such as textile, dyeing, paper, printing, colour photography, pharmaceutical, food, cosmetics, and electronics, (Naveenraj *et al.*, 2013). These industries constitute major sources of dye environmental pollution, their effluents are highly coloured and the disposal of these waste into the environment can be extremely deleterious (Ozer *et al.*, 2005). Reports show that over 100,000 dyes are commercially available and approximately 10-15% of them are lost to waste stream during the colouration process (Ratna and Padhi, 2012); most of these dyes are difficult to decolourise due to their complex aromatic molecular structure and are stable to heat, light, water and oxidising agents (Jaikmumar *et al.*, 2009). They are known to be carcinogenic and mutagenic in nature and can cause the non-acceptability of drinking water supplies (Jadhav *et al.*, 2007). Dyes may also undergo degradation to form products that are highly toxic and carcinogenic (Aksu, 2005; Chen, 2006 and Alaguprathana and Poonkothai, 2017). The discharge of certain dyes into rivers and lakes also results in a reduced dissolved oxygen concentration causing anoxic conditions, which subsequently affect aerobic organisms (Chander and Arora, 2007). Hence there is the need to seek a cost-effective and simple way of removal of such toxic chemicals.

Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of colouring materials (Jain *et al.*, 2003; Ho and McKay, 2003; Derbyshire *et al.*, 2001). However, the adsorption process is influenced by the nature of the adsorbate and its substituent groups. The presence and concentration of surface functional groups play an important role in the adsorption capacity and the removal mechanism of the adsorbate (Azraa *et al.*, 2012). Most commercial systems currently use activated carbon as a sorbent to remove dyes in wastewater because of its excellent adsorption ability and it is one of the best available control technologies as cited by the US Environmental Protection Agency (Derbyshire *et al.*, 2001). Most of these dyes such as Reactive Violet 5 and Direct Red 23 are not easily degraded and often not removed through conventional treatment methods such as

the activated sludge method and filtration. Although activated carbon is a preferred sorbent, its widespread use is restricted due to its high cost. To decrease the cost of effluent treatment, it is, therefore, necessary to find inexpensive alternative adsorbents. One of such alternatives could be obtained from biological materials like agricultural residues and fungal biomass. Also, mathematical models such as the Langmuir isotherm, Freundlich isotherm, Sips, and Redlich-Peterson isotherms, Intra-particle diffusion, pseudo-second-order, Elovich, and Power function kinetic models have been used to investigate the efficiency of biosorption processes of dyes on adsorbents (Volesky, 2003; Akar et al., 2009; Colak *et al.*, 2009; Mittal *et al.*, 2014; Sanda et al., 2017). This research seeks to evaluate the possibility of getting a biological adsorbent that can serve as a substitute for activated carbon and possibly realign industrial and public ways of using and discharging dye-treated materials, knowing that agricultural materials are easily available and cost-effective. The present study aims to determine the adsorption capacity and effect of treatment on the adsorption properties of pig waste.

II. MATERIALS AND METHODS

A. Chemicals and reagents

The following chemicals and reagents were procured for the study: Reactive Violet 5 (Sigma Aldrich Germany), Triton X₁₀₀, Sodium Dodecyl Sulphate (SDS) (Sigma Chemicals Co., Germany); Hydrochloric acid (BDH, England), Sodium hydroxide pellets (Qualikems Fine Chemicals PVT. Ltd, New Delhi India). All other chemicals used were of analytical grades.

B. Collection of biological materials used as adsorbents

The biological material used as adsorbents, pig waste was obtained from a local farm at Akwa-Akuma, Owerri, Nigeria. The pig waste was collected as dry animal droplets into sterile containers and transported to the laboratory for the study.

C. Preparation of adsorbents

One hundred grams (100g) of freshly collected pig wastes were put into three different transparent open containers saturated with water and left in the open air for three months. The composted wastes were later air-dried at room temperature ($28 \pm 2^{\circ}\text{C}$) following its complete decay evidenced by reduced smell. Thereafter, the composted materials were ground in a mortar and sieved with a 100 μm sieve to obtain particles of size 0.1m. The composted, untreated, and dried agricultural wastes were labeled pig dung (PGD) and stored in airtight containers at room temperature for the study.

D. Modification and activation of pig waste

One hundred grams of the pig wastes were subjected to chemical activation using Triton X100 (TX100) and 1% sodium dodecyl sulphate (SDS) according to the methods described by Chatterjee *et al.*, (2009). For each treatment, 50g each of the composted wastes was weighed into 300mls of 0.1% Triton X100 or 1g/l SDS in distilled water in a 500ml conical flask. These were properly mixed by stirring to obtain a homogeneous mixture of the materials. This was

allowed to stand for 30mins. Thereafter, the treated waste was filtered and subsequently washed thrice with deionized water. The adsorbents were spread on glass Petri dishes and oven-dried at 60°C for 12hrs. Thereafter, the dried adsorbents were ground in a mortar and sieved using a 100 μm sieve. The treated agricultural wastes were tagged as PGD-TX100 and PGD-SDS. The adsorbents were then cooled in a desiccator and stored in air-tight plastic bottles for further use.

E. Preparation of acidified and basified water

Acidified and basified water of pH ranges of 1-10 was prepared by acidifying deionized water with 0.1M HCl for pH 1.0 – 6.0 or 0.1M NaOH for pH 7.0 - 10 to obtain water at each of the pH values. The final pH was adjusted accordingly by drop-wise additions of either 0.1M NaOH or 0.1M HCl.

F. Determination of the effect of pH on dye removal capacity by adsorbents

To 90ml of deionized water at different pH ranges (1-10), each contained in 100ml volumetric flasks were added 10ml of the dye stock (1000mg/l). This contained dye-solution in different pH ranges (1-10) at 100mg/l and was referred to as stock B1 to B10 to represent the different pH ranges. Some 0.2g of the respective adsorbent powder was weighed into ten separate 100ml conical flasks containing 9ml of water at different pH ranges (1-10). Thereafter, 1ml of the dye solution from the stock concentration (100mg/l) was added to each of the flasks. The mixtures were homogenized by shaking the flasks on an automatic rotator (model: D97980, Marienfeld Germany) for 2h at 150rpm. After homogenization, the dye-adsorbent solutions were centrifuged in a test tube at 4000rpm (Uniscop laboratory centrifuge model: SM112, Surgifriend medicals England) for 10mins and the supernatant was collected using a clean and dried 5ml glass pipette. The absorbance of the supernatant was determined using the spectrophotometer (Turner, model 390) at 575nm.

The adsorption capacity was evaluated using the formula according to Jaikumar *et al.*, 2009;

$$Q_e = \frac{C_o - C_e}{M} \times V \quad (1)$$

Absorption capacity (Q_e) = Maximum dye uptake was calculated as shown above.

Where C_o = initial dye concentration (100mg/l) used for the adsorption

C_e = Equilibrium dye concentrations in solution (10mg/l);

V = the dye volume used (0.1ml),

M = the adsorbent mass (0.2g).

$$\text{Percentage sorption} = \frac{Q_e}{Q_{e(\text{max})}} \times 100. \quad (2)$$

G. Determination of the effect of dye concentration on dye removal capacity of the adsorbent

This analysis was done to determine the amount of dye removed (%) by the adsorbent materials (treated and untreated agricultural wastes) at different dye concentrations. Dye concentrations of 50-1000mg/L were used in the study. Some 0.2g of the adsorbent materials (treated and untreated agricultural wastes,) was introduced into 10ml of the different concentrations of dye-solution at pH1 in 20ml test tubes. The mixtures were homogenized and allowed to stand on a rotary shaker for 2 hours at 150rpm under room temperature of $28\pm 2^\circ\text{C}$. Thereafter, the dye-adsorbent solution was centrifuged at 4000rpm for 10min. The supernatant sample was carefully withdrawn and the absorbance was determined spectrophotometrically at 575nm wavelength. The adsorption capacity was evaluated using the formula of Jaikumar *et al.*, 2009:

H. Determination of the effect of time on dye removal capacity of the adsorbent

This analysis was done to obtain the minimum time required for effective dye adsorption. Some 0.2g of the respective adsorbent powders were weighed separately into 100ml conical flasks containing 10ml of 100mg/l RV5 solution of pH 1. The mixtures were homogenized by shaking on a rotator shaker (model: D97980, Marienfeld Germany) at 150rpm for time intervals of 5, 30, 60, 80, and 180 minutes. After each stipulated time, the dye-adsorbent solutions were collected and centrifuged in a test tube at 4000rpm for 10mins. The supernatant was collected using a clean grease-free dried pipette. The supernatant sample was carefully withdrawn and the absorbance was determined spectrophotometrically at 575nm wavelength. The amount of dye removed was estimated by comparing with the initial dye concentration absorbance at the time: 0, 5, 10, 30, 60, 120, and 180mins respectively, and estimated using the formula described by Jaikumar *et al.*, 2009.

I. Data analysis and mathematical modelling

The linear and non-linear equation models were also used to measure and ascertain the adsorption capacity of RV5 with time. The data obtained from this study were analyzed by using the pseudo-second-order, intra-particle diffusion, Elovich, and power function kinetic equation models to examine the rate of the adsorption process.

J. The pseudo second order kinetic rate equation is expressed as follows:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

Equation (3) is linearized as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where q_t is the amount of RV5 adsorbed (mg/g) at equilibrium and k_2 is the equilibrium rate constant of pseudo-second-order sorption ($\text{gmg}^{-1}\text{min}^{-1}$).

The q_e and k_2 are determined from the slope and intercept of t/q_t versus t plot (Koyuncu *et al.*, 2011). The kinetic parameter values from the linear plots were used as initial estimates to estimate the parameters from the non-linear model.

The intraparticle diffusion rate model (Karagöz *et al.*, 2008) is expressed as:

$$q_t = K_{\text{dif}} t^{1/2} + C \quad (5)$$

Where K_{dif} is the rate constant ($\text{mg g}^{-1} \text{mins}^{-0.5}$) and C is the intercept. If intra-particle diffusion occurs, then q_t against $t^{1/2}$ will be linear with slope K_{dif} and the line will pass through the origin if the intra-particle diffusion was the only rate-limiting parameter controlling the process. Otherwise, some other mechanism is also involved.

The Elovich kinetic model equation is also given as:

$$q_t = \frac{\text{Ln}(\beta\alpha t)}{\beta} \quad (6)$$

Its linearized form is given as:

$$q_t = \frac{\text{Ln}\beta\alpha}{\beta} + \frac{\text{Lnt}}{\beta} \quad (7)$$

Where q_t is the amount of dye adsorbed by sorbate at a time t , α is the initial adsorption rate constant (mg/g min) and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The power function model is a modified form of the Freundlich equation and may be expressed by equation (9) (Ho and McKay, 2002) and its linear form as given in equation (9). The power function kinetic equation is expressed as:

$$q_t = at^b \quad (8)$$

K. Equation (9) is linearized as:

$$\text{Log } q_t = \text{Log } a + b \text{ log } t \quad (9)$$

Where q_t is the amount of dye sorbed by the sorbent at a time t , while a and b are constants with $b < 1$. The function b is also a constant, being the specific sorption rate at the unit time when $t = 1$.

The equilibrium data were fitted to adsorption isotherm models; Langmuir, Freundlich, Redlich-Peterson, and Sips models.

L. Langmuir equation given as:

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \tag{10}$$

Where q_o is the maximum adsorption capacity (mg/g) and K_L is the equilibrium adsorption coefficient (l/mg) related to the free energy of adsorption. C_e is the equilibrium concentration of Reactive Violet 5 in the aqueous solution and q_e is the equilibrium adsorption capacity of the adsorbent.

The linearized form of the Langmuir equation can be written as:

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_L} \cdot \frac{1}{C_e} \tag{11}$$

The Langmuir constant q_o and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$.

The Freundlich model is an empirical equation on sorption on the heterogeneous surface. It is given as:

$$q_e = K_f C_e^{1/n} \tag{12}$$

Where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity respectively. The linearized form of Freundlich isotherm can be written as:

$$\text{Ln}q_e = \text{Ln}K_f + \frac{1}{n} \text{Ln}C_e \tag{13}$$

The value K_f and n can be calculated by plotting $\text{Ln}q_e$ and $\text{Ln}C_e$. The values of q_o , K_L , and n obtained from the linear models are used as initial estimates to estimate their values with non-linear models using an iterative method.

Redlich- Peterson isotherm (R-P) contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms into a single equation.

The general isotherm equation of the Redlich-Peterson model is given as:

$$q_e = \frac{q_{mon} \beta_{RP} C_e}{1 + \beta_{RP} C_e^\alpha} \tag{14}$$

The linearized form of the isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{\beta_{RP} q_{mon}} + \frac{1}{q_{mon}} C_e^\alpha \tag{15}$$

Where q_{mon} is the Redlich–Peterson model isotherm constant, β_{RP} the Redlich–Peterson model constant; β_{RP} the Redlich–Peterson model exponent

The Sips isotherm is given as:

$$q_e = \frac{q_{max} K_S C_e^{1/n}}{1 + K_S C_e^{1/n}} \tag{16}$$

Its linearized form is given as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_S} \cdot \frac{1}{C_e^{1/n}} \tag{17}$$

Where K_S is the Sips constant related with an affinity constant (mg l^{-1}) $1/n$ and q_{max} is the Sips maximum adsorption capacity (mg g^{-1}).

RESULTS AND DISCUSSION

A. Effect of pH on dye removal capacity of adsorbents

The results revealed that the biosorption of RV5 was strongly dependent on the pH of the solution. The effect of pH was studied at a pH 1.0 – pH 10. The maximum removal capacity for each of the adsorbents was found to be at pH 1 as shown in figures 1. The dye removal capacity decreased with increasing pH from 1-3 for SDS and TX100 treated PGD. The RV5 sorption remained relatively constant in the pH ranges of 4.0-10.0 studied for each of the adsorbents.

B. Effects of time on dye removal capacity of the adsorbents

The effect of time on adsorption of RV5 was investigated as shown in figure 2. The adsorption capacity increased with increasing adsorbent concentration. The dye removal efficiency was very rapid during the initial stages of the adsorption process followed by a gradual steady-state increase before equilibrium was attained. Equilibrium time was found to be 80mins for different adsorbent materials, and the adsorption capacity at the equilibrium time was 45%, 48%, and 70% for untreated, TX100 and SDS treated PGD. Agricultural wastes treated with SDS showed a relatively higher adsorption capacity up to 70% when compared to untreated and TX100 treated.

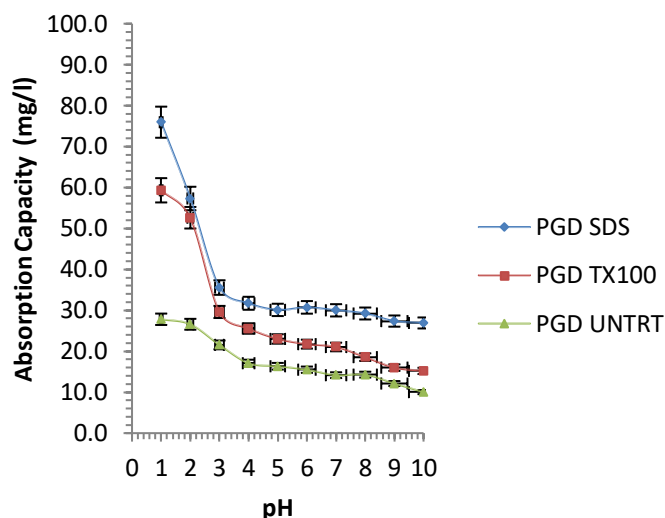


Fig. 1: Effect of pH on the adsorption of RV5 on composted PGD

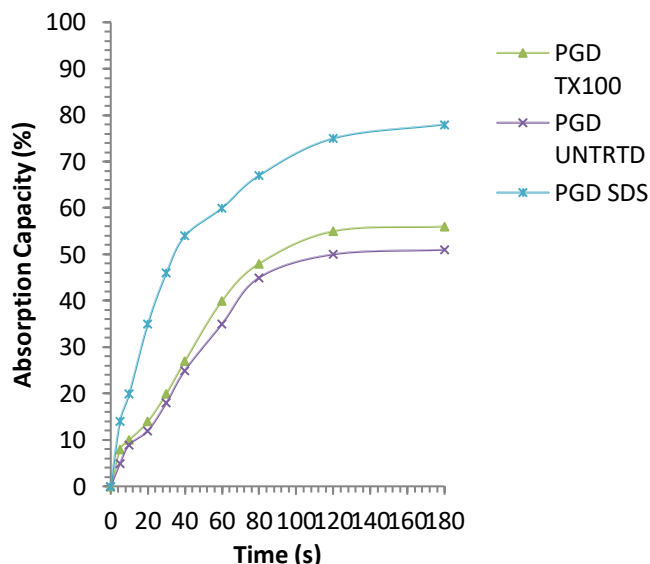


Fig. 2: Effect of time on the adsorption of RV5 on composted PGD

C. Effects of time on dye removal capacity of the absorbents using pseudo-second-order linear model and Intra particle diffusion linear kinetic model

The pseudo-second-order linear model (figure 3a) and Intra particle diffusion linear kinetic model (figure 3b), show a highly significant correlation of absorption capacity with time ($R^2 > 0.7$). The results for the effect of time on the adsorption of reactive violet 5 on composted pig wastes treated with Triton X-100 and SDS at 50 mg/l are shown in figures 1a; the values of kinetic parameters q_e and K_2 , for the pseudo-second-order models are presented in table 1. The intraparticle diffusion linear kinetic model also showed a significant correlation of absorption capacity with time ($R^2 > 0.7$). The experimental data obtained closely fitted into the intraparticle diffusion linear kinetic model with a non-zero y-axis intercept (Figure 3b). The equation of the relationship are presented on the charts and correlation coefficients (R^2)

values obtained are 0.999, 0.999, and 0.999 for SDS, TX100, and untreated using the pseudo-second-order linear model; for Intra particle diffusion linear kinetic model (R^2) values was 0.847, 0.882 and 0.739 for SDS, TX100 and untreated respectively, indicating a strong fit of experimental kinetic data to the models.

D. Effects of time on dye removal capacity of the absorbents using power function linear kinetic model and Elovich linear kinetic model

Linearization of power function kinetic models shows a good fit of experimental data into the model for adsorption capacity and adsorption time for the absorbent PGD treated with TX100 and SDS. The effect of time on the adsorption of Reactive Violet 5 on composted pig wastes treated with Triton X-100, SDS, and untreated at 50 mg/l are presented in figure 4a. The equation of the linear relationship is

presented on the charts and correlation coefficients (R^2) values obtained are significant ranging from 0.8-0.965 indicating a strong fit of experimental kinetic data to the model.

The Elovich linear kinetic model also showed a significant correlation of absorption capacity with time ($R^2 > 0.9$). The results for the effect of time on the adsorption of Reactive Violet 5 on composted pig wastes treated with

Triton X-100, SDS, and for untreated at 50 mg/l are shown in figure 4b. Experimental data obtained closely fitted into Elovich linear kinetic with a non-zero y-axis intercept. The results are shown for Tx100, SDS treated, and untreated PGD. The equation of the relationship is presented on the charts and correlation coefficients (R^2) values obtained are significant ranging from 0.9-0.968 indicating a strong fit of experimental kinetic data to the model.

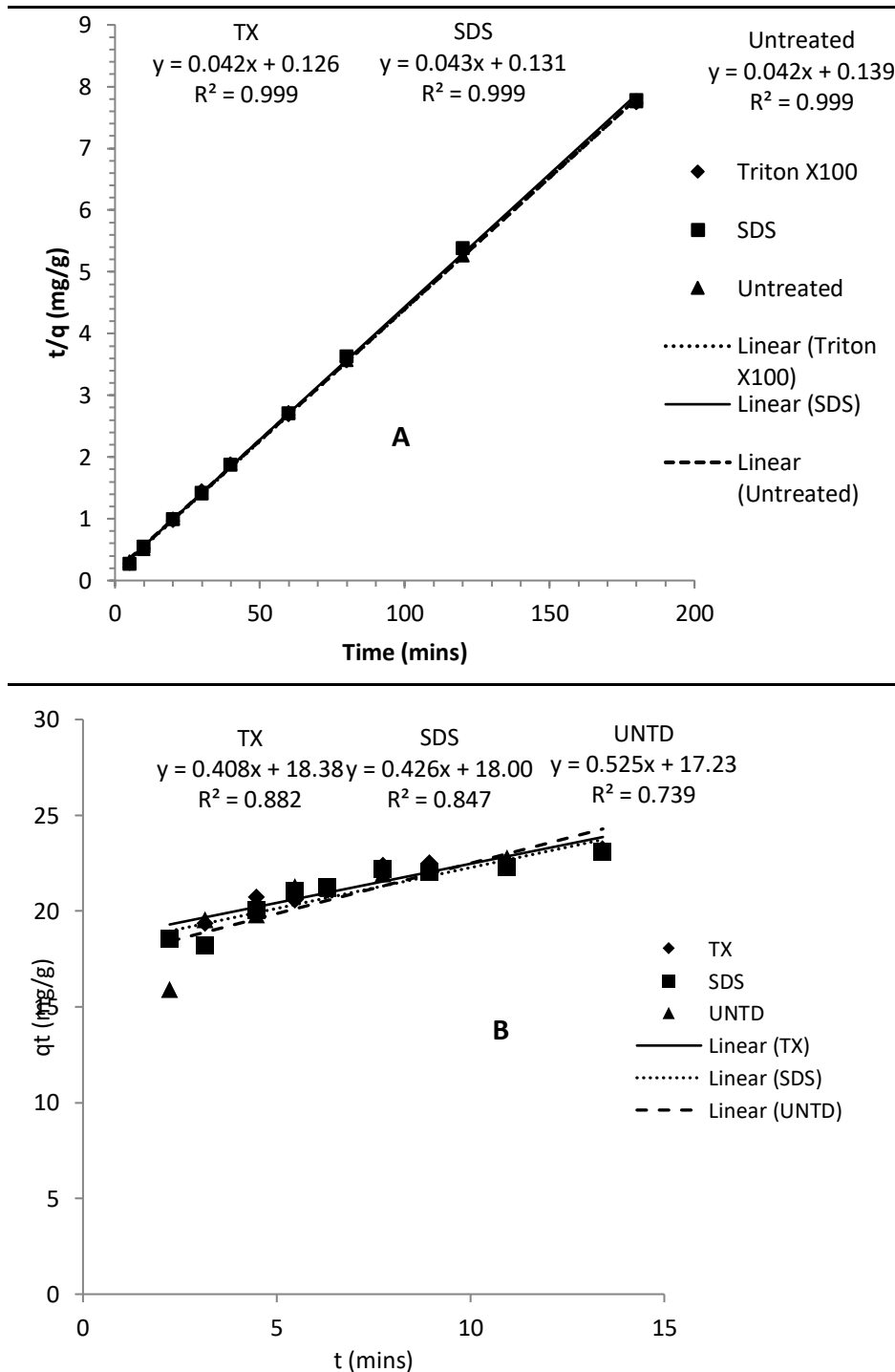


Fig. 3: Pseudo-second-order linear kinetic (a) and Intra particle diffusion linear kinetic modeling (b) of the effect of time on the adsorption of reactive violet 5 on composted pig waste treated with Triton X-100 and SDS.

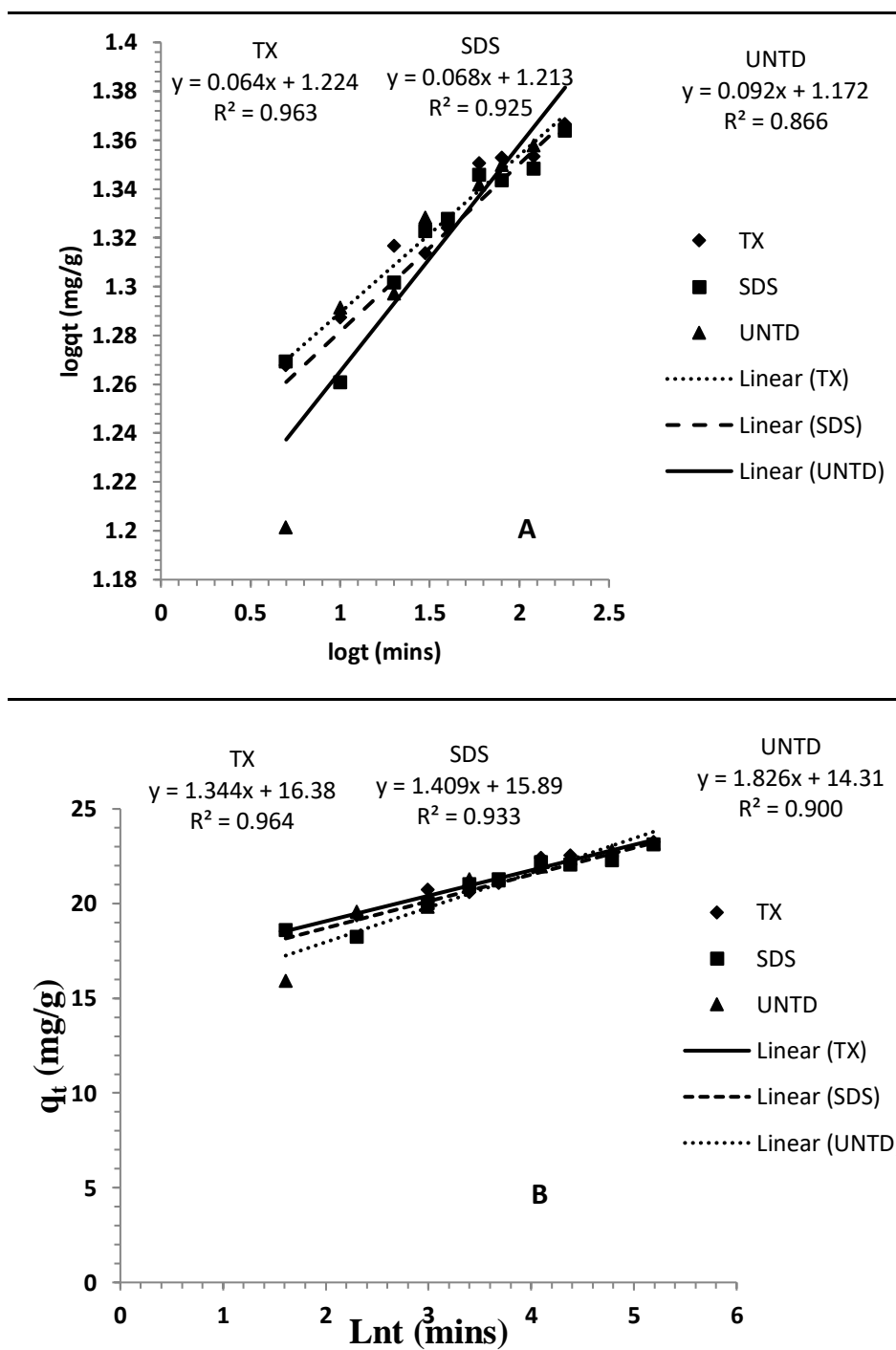


Fig. 4: Power function linear kinetic(A) and Elovich linear kinetic modeling (B) of the effect of time on the adsorption of Reactive Violet 5 on composted Pig waste treated with Triton X-100, SDS, and untreated

E. Effects of dye concentration on dye removal capacity of the absorbents using Langmuir and Freundlich Isotherms

The linear plots of Langmuir Isotherm for adsorption of RV5 on composted pig waste treated with Triton X-100 and SDS showed that adsorption of RV5 by SDS treated PGD and untreated closely fitted into the linearized form of Langmuir Isotherm; while the TX100 treated waste adsorption was not consistent with Langmuir isotherm. The correlation coefficient (R^2) were 0.915, 0.816, and 0.916 for SDS, TX100, and untreated PGD respectively (Figure 5a).

The linear plots of Freundlich Isotherm for adsorption of Reactive Violet 5 on composted pig waste, showed that adsorption of RV5 by PGD treated with SDS and TX100 strongly aligned with a linearized Freundlich Isotherm for the effect of dye concentration on adsorption capacity; with a high correlation coefficient (figure 5b). The correlation coefficient (R^2) were 0.968 and 0.937 for the PGD treated with SDS and TX100 respectively. The adsorption of RV5 by untreated PGD with R^2 value of 0.570 was not describable by Freundlich Isotherm. The model kinetic parameters are presented in table 1.

F. Effects of dye concentration on dye removal capacity of the absorbents using Redlich-Peterson Isotherm and SIPS Isotherm

The linear plot of Redlich-Peterson Isotherm (Figure 6a) and SIPS Isotherm (figure 6b) for adsorption of Reactive Violet 5 onto composted pig waste treated with Triton X-100 and SDS showed that adsorption of RV5 by PGD treated with SDS and TX100 strongly aligned with a linearized Redlich-Peterson Isotherm and SIPS Isotherm

with a high correlation coefficient. The experimental data fitted into the model with intercept closely approaching zero. The correlation coefficient (R^2) for Redlich-Peterson Isotherm was 0.930, 0.867, and 0.987 for the absorbent PGD treated with SDS, TX100, and untreated respectively. While the correlation coefficient (R^2) for SIPS Isotherm was 0.989, 0.941, and 0.915 for SDS, TX100, and untreated respectively. The model kinetic parameters are presented in table 1.

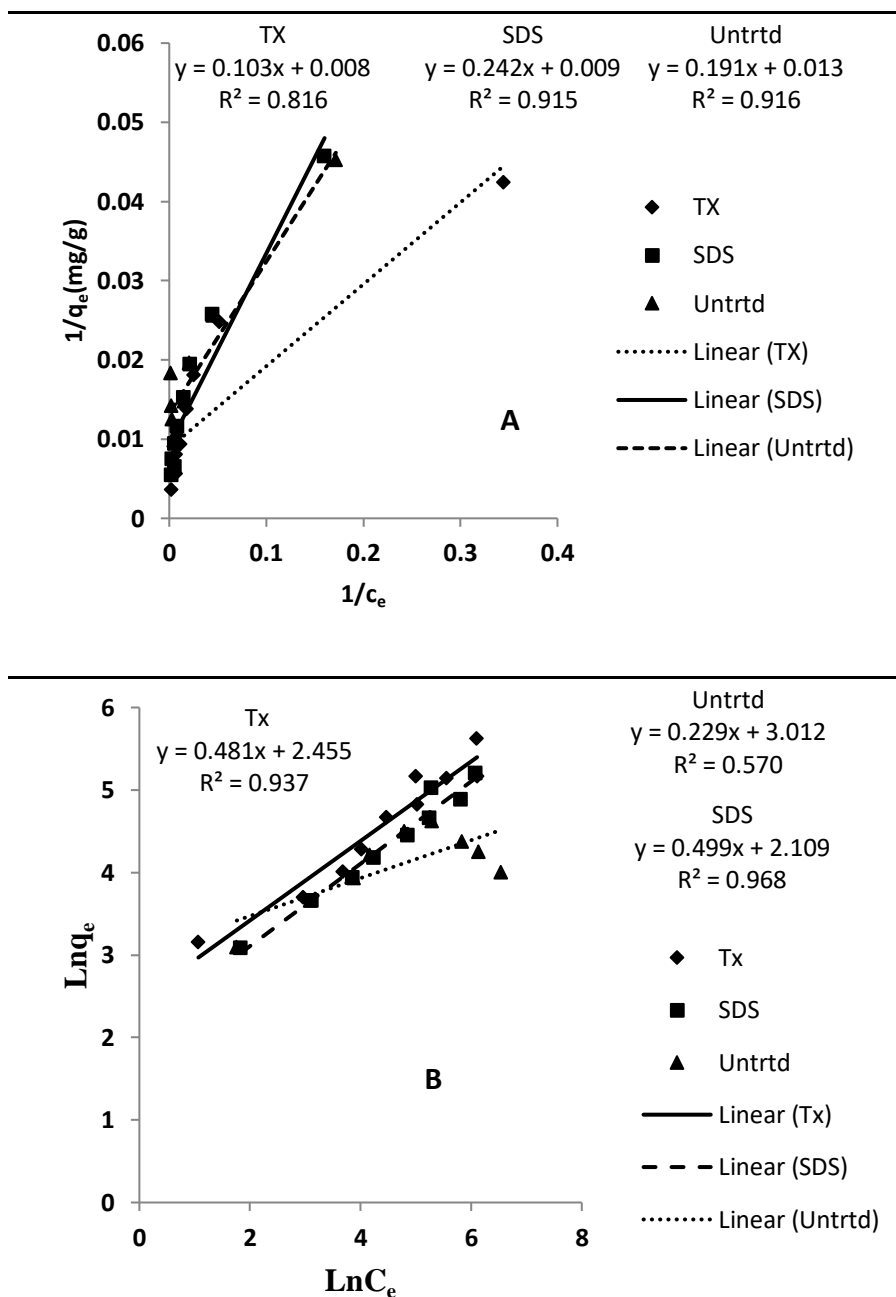


Fig. 5: Linear plot of Langmuir Isotherm (A) and Freundlich Isotherm (B) for the adsorption of Reactive Violet 5 onto composted pig waste treated with Triton X-100, SDS and untreated.

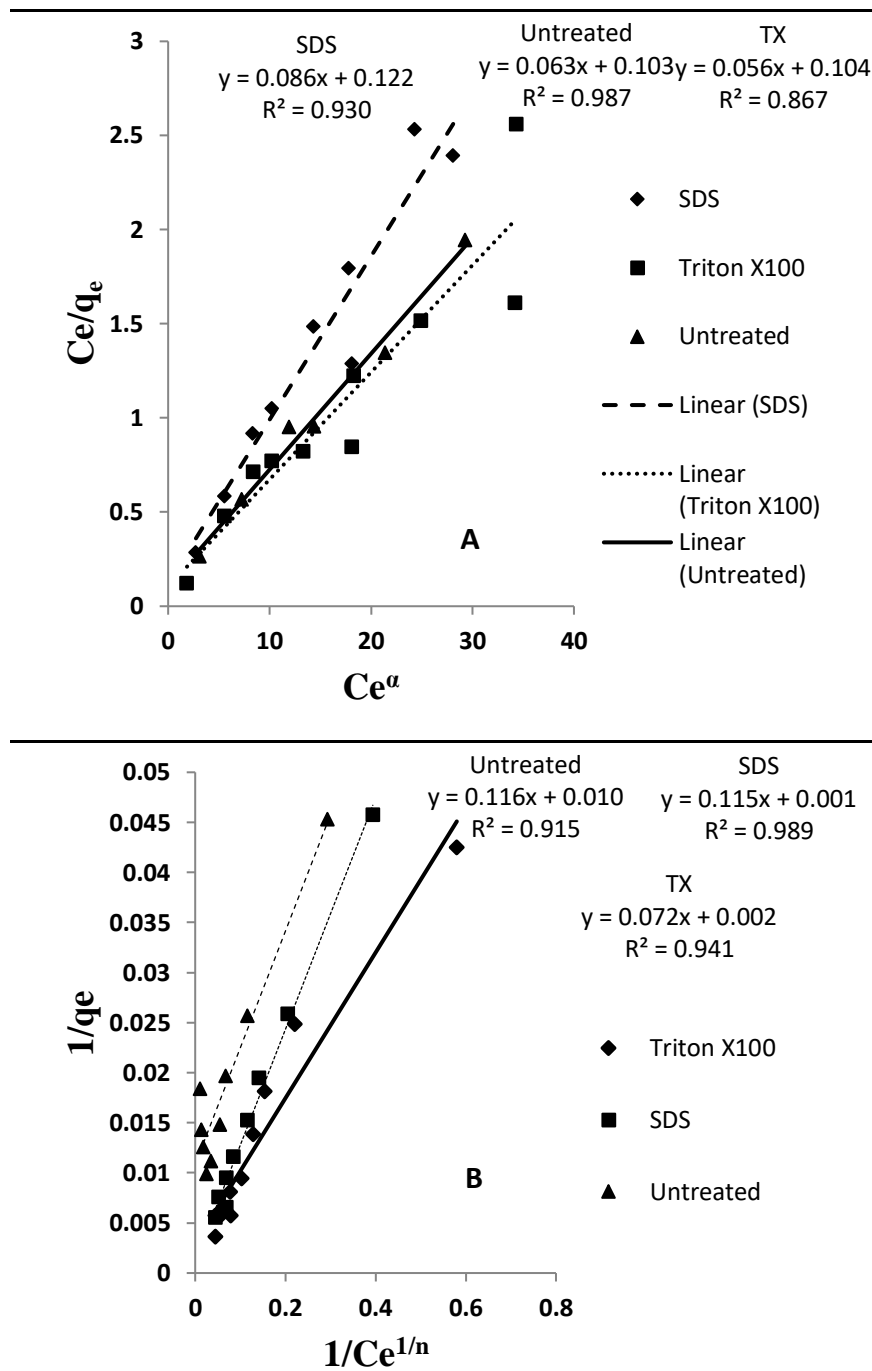


Fig. 6: Linear plot of Redlich-Peterson Isotherm (A) and SIPS Isotherm (B) for the adsorption of Reactive Violet 5 onto composted pig waste treated with Triton X-100, SDS, and untreated

G. Non-linear Freundlich isotherm model of the effect of dye concentration on dye removal capacity of the adsorbents

The results obtained revealed that the biosorption of RV5 onto composted pig waste treated with Triton X-100 and SDS was strongly dependent on the dye concentration as it greatly influenced the adsorption capacities of the adsorbents. The effect of dye concentration on dye removal capacity of the adsorbents studied at 0.2g of the respective adsorbent materials showed that adsorption of RV5 dye decreased as dye concentrations increased from 50mg/l to 1000mg/l as shown in figures 5. The non-linear plots for adsorption of Reactive violet 5 onto the respective

adsorbents were fitted into Freundlich Isotherm models as shown in Figure 7 a, b, c. respectively. The Freundlich kinetic correlation coefficients (R^2) values are 0.8913 and 0.9879, for adsorbent materials treated with Triton X-100 and SDS respectively.

H. Adsorption isotherm constants of mathematical models of the effect of dye concentration and time on dye removal capacity of the adsorbents

Table 1 shows the adsorption isotherm constants of mathematical modelling of the effect of time on dye removal capacity of the adsorbents PGD treated with TX100, SDS, and untreated. The effect of time on adsorption capacity

was modelled using Pseudo-second-order Kinetic, Intraparticle Diffusion rate Model, Elovich Kinetic Model, Power Function, Langmuir Equation, Redlich-Peterson Isotherm, and Sips Isotherms; these models showed a significant correlation of adsorption capacity with time for the TX100 and SDS treated sample than the untreated; with R^2 values ranging from 0.7-0.999 (Table 1). The effect of

dye concentration on adsorption capacity was modelled using Freundlich Model; the relationship was linear and yielded a strong correlation between dye concentration and adsorption capacity with R^2 values of 0.937 and 0.968 compared to 0.570 for untreated (Table 1). The kinetic parameters are presented in the table 1

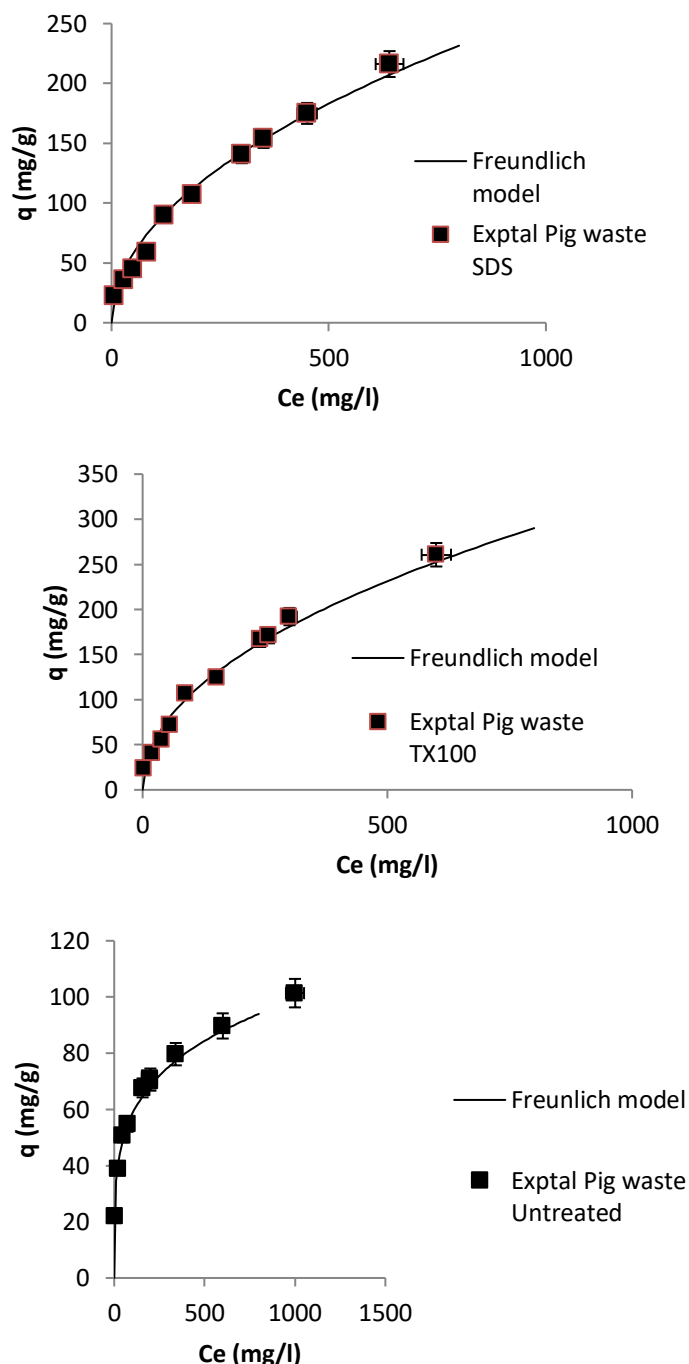


Fig. 7: Non-linear modeling of the effect of dye concentration on dye removal capacity of composted pig waste treated with SDS, TX100 and untreated using Freundlich Isotherms

| Adsorption Models | | Adsorbents | | |
|--|--------------|------------------|------------------|----------------|
| | | PGD | | |
| Pseudo-second-order Kinetic | Treatment | Qe | K ₂ | R ² |
| | TX100 | 23.81 | 0.01 | 0.999 |
| | SDS | 23.26 | 0.01 | 0.999 |
| | UNTR | 23.81 | 0.01 | 0.999 |
| Intra-particle Diffusion rate Model | | Kdif | C | |
| | TX100 | 0.41 | 18.38 | 0.882 |
| | SDS | 0.43 | 18.00 | 0.847 |
| | UNTR | 0.53 | 17.23 | 0.739 |
| Elovich Kinetic Model | | β | α | |
| | TX100 | 0.74 | 263853.75 | 0.964 |
| | SDS | 0.71 | 111344.25 | 0.933 |
| | UNTR | 0.55 | 4623.60 | 0.900 |
| Power Function | | b | a | |
| | TX100 | 0.06 | 16.75 | 0.963 |
| | SDS | 0.07 | 16.33 | 0.925 |
| | UNTR | 0.09 | 14.86 | 0.866 |
| Langmuir Equation | | KL | Q0 | |
| | TX100 | 0.08 | 125.00 | 0.816 |
| | SDS | 0.04 | 111.11 | 0.915 |
| | UNTR | 0.07 | 76.92 | 0.916 |
| Freundlich Model | | n | Kf | |
| | TX100 | 2.08 | 11.65 | 0.937 |
| | SDS | 2.00 | 8.24 | 0.968 |
| | UNTR | 4.37 | 20.33 | 0.570 |
| Redlich-Peterson Isotherm | | Q _{mon} | β _{RP} | |
| | TX100 | 11.63 | 0.70 | 0.930 |
| | SDS | 15.87 | 0.61 | 0.987 |
| | UNTR | 17.86 | 0.54 | 0.867 |
| Sips Isotherms | | K _s | Q _{max} | |
| | TX100 | 0.03 | 500.00 | 0.941 |
| | SDS | 0.09 | 1000.00 | 0.915 |
| | UNTR | 0.01 | 100.00 | 0.989 |

Table 1: Adsorption isotherm constants of adsorbents

III. DISCUSSION

The present study evaluated adsorption characteristics, diffusion, and isotherms of modified pig waste for removing reactive violet 5. In the study, biosorption of RV5 was strongly pH-dependent. The effect of pH indicated that the maximum dye removal efficiency of the adsorbents was achieved around pH 1. Treatment of the adsorbent resulted in a significant increase in adsorption capacities, SDS and triton-x 100 treated pig competed effectively with activated charcoal in the adsorption of RV5. SDS and TX100 treatment of PGD resulted in adsorption capacities of 76mg/l and 60mg/l respectively.

The extent of adsorption of the dye decreased with increasing pH for AC, treated, and untreated PGD adsorbent. An increase in pH from pH 1-3, caused a rapid decrease in adsorption capacity of untreated and treated PGD adsorbents. RV5 adsorption remained relatively unaffected in the pH ranges of 4.0-10.0 for these adsorbents. The observed optimal removal of RV5 at Low pH of 1-2 may be attributed to an increased protonation of dye by the acidic medium. This results in the saturation of the dye surface with positive charges; which creates a strong electrostatic attraction with PGD adsorbent surface, saturated with negatively charges provided by treatment with anionic SDS. This provides a strong electrostatic attraction for the removal of anionic RV5. This may also be

responsible for a more enhanced absorptive capacity of SDS treated samples compared to TX100. TX-100 is non-ionic and may not strongly impact the surface charge of adsorbent. The pH value of the dye solution plays important role in the adsorption process, specifically impacting adsorption capacity. The net charge of a dye solution is proportional to the pH of the solution surrounding the dye particles (Allen and Koumanova, 2005). Furthermore, lower adsorption of RV5 dye beyond pH 3 may be explained by a lower electrostatic interaction between the dye and adsorbent resulting from the presence of excess OH⁻ ions on the surface of the anionic RV5 dye. The decreased interaction with PGD adsorbent surface saturated with negative charges is provided by treatment with anionic SDS. The trend of adsorption of RV5 indicates that the unprotonated form of the dye is not readily adsorbed on the surface of our SDS and TX-100 treated PGD. Similar results have been reported in the studies of Kumar *et al.*, 2010 for adsorption of Congo red dye on cashew nutshell. Also, the works of Pavan *et al.*, 2008, reported a similar trend for removal of Congo red by aniline propylsilica xerogel, sunflower seed hull (Thinakaran *et al.*, 2008), and removal of Congo red using Jujuba seeds (Reddy *et al.*, 2012). Hashemian *et al.*, (2013) reported that the lowest adsorption of RV5 using activated carbon developed from orange Peel occurs at pH 2.0 and the greatest at pH > 7.0. This disparity observed may be due to the difference in the adsorbent material and the chemical activation of adsorbent material to modify charges on the surface.

Also, our study revealed that adsorption of RV5 was strongly dose-dependent. The fitting of experimental data into the Freundlich model revealed a consistent increase in the adsorption capacity of the adsorbents. The amount of dye adsorbed increased with a higher concentration of the dye in solution from 50mg/l to 1000mg/l. This pattern of adsorption was consistent with untreated and treated forms of PGD adsorbents. Comparison of the potential of the adsorbents indicated a higher adsorption capacity in treated SDS treated than TX100 treated PGD. This may be attributable to an intrinsic property of the dye such as van der Waals interaction, dipole-dipole, and hydrogen bonding between dye molecules. Freundlich model has been reported to best fit experimental data of SDS activation of adsorbent (Al-Asheh *et al.*, 2003).

Non-linear kinetic modeling of the effect of time on the adsorption of Reactive Violet 5 using pseudo-second-order model, power function model, and Elovich model showed that dye removal efficiency was very rapid during initial stages of adsorption process followed by slow increase with an increase in time. At higher contact time, the rate of adsorption decreased and a saturation stage was reached. At this point equilibrium was attained, a saturation of adsorbent surface occurs, and a further increase in exposure time resulted in no net changes in the amount of dye adsorbed. This decline is due to a decrease in total adsorbent surface area and increased diffusion pathway (Hameed *et al.*, 2008; Singh *et al.*, 2009). Equilibrium time was found to be approximately 30 minutes for 50 mg/l of dye solution for treated and untreated adsorbents in this

study. Similar results have been reported in the studies of Toor and Jin, (2012), Lian *et al.*, (2009).

The experimental data obtained in this study tightly fitted into pseudo-second-order, power function, and Elovich non-linear kinetic models with significant correlation coefficients expressing a significant correlation of adsorption capacity with time. These models satisfactorily described the equilibrium behavior of RV5 dye based on the high values of the correlation coefficients. It is also important to note that linear fitting of experimental data using pseudo-second-order model, and Elovich model, strongly corroborates with trends of non-linear models of this equation. The values of correlation coefficient were very high ($R^2 \geq 0.995$) for pseudo-second-order model and Elovich linear model and ($R^2 \geq 0.85$) for Power function linear model. The theoretical kinetic parameters obtained, from this model were closer to the experimental at different initial RV5 concentrations. It may be assumed that the pseudo-second-order model and Elovich linear model best describe the adsorption behavior of SDS and TX100 treated PGD for RV5 at equilibrium.

The Kinetics of PGD adsorption showed that using the intra-particle diffusion model, adsorption closely fitted into a non-zero intercept straight-line form with high correlation coefficients range of $R^2 \geq 0.79$ for the different adsorbents. This however is indicative of a multi-path diffusion mechanism being involved in the adsorption of RV5 by treated and untreated. The intraparticle diffusion model describes the transport of adsorbate molecules to occur in macropores, transitional pores, and micropores (Koumanova *et al.*, 2003). The sorption rate is known to be controlled by several factors including; diffusion of the solute from the solution to the film surrounding the particle, diffusion from the film to the particle surface, diffusion from the surface to the internal sites, and uptake which can involve several mechanisms such as Physico-chemical sorption, ion exchange, precipitation or complexation (Gercel *et al.*, 2007, Wu *et al.*, 2001). Therefore, we may assert that the rate of attainment of equilibrium adsorption of RV5 by PGD-SDS and PGD-TX100 may be particle-diffusion controlled (Yang *et al.*, 2005).

The Langmuir isotherm assumes that the surface of any adsorbent material contains a fixed number of identical homogeneous and energetically equivalent active sites; saturation of these active sites stops the adsorption of the adsorbate. This indicates that the adsorption occurs until a monolayer of adsorption is completed and after completion of adsorption, further interaction of adsorbent and adsorbate molecules ceases (Mittal *et al.*, 2009, Li, *et al.*, 2009, Colak *et al.*, 2009). In the present study, the Langmuir maximum adsorption capacity (Q_0) was 125.00, for PGD-TX100, and 111.11 for PGD-SDS; indicating adsorption efficiency to be in the order PGD-TX100 > PGD-SDS. Fitting of experimental data of adsorption of RV5 by PGD-SDS, and PGD-TX100 and untreated forms were significant with high correlation coefficient values. The Correlation coefficient of Langmuir fits was in the range 0.79-0.95 for the different adsorbents.

Furthermore, analysis of experimental data using Freundlich models indicated a stronger fit of data into the model than the Langmuir model. The Freundlich model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption (Colak *et al.*, 2009, Volesky, 2003). The favourability and the nature of the adsorption process can be identified from the value of the constant n . In the present study, the value of n was all greater than 1 (table 1), indicating that the adsorption process was favorable. Therefore, The Freundlich model in both linear and non-linear form yielded a better fit to experimental data. The high values of R^2 (>0.95) suggested the Freundlich model to best describe the adsorption process.

Furthermore, the results of the present study also demonstrated a good fit of experimental data with the Redlich–Peterson isotherm model and SIPS Isotherms. The Redlich–Peterson isotherm model presented high correlation coefficient values of $R^2 \geq 0.93$ for SDS and TX100 treated samples. Treatment of PGD with SDS and TX100 increased β_{RP} constants of the isotherm, indicating a higher adsorption capacity of the treated sample compared to the untreated sample (table 1). The Redlich–Peterson isotherm model is a hybrid that combines elements from both the Langmuir and Freundlich equations. Similar trends were also observed using fits of the Sips isotherm. In the Sips isotherm, K_s deviated widely from unity which again denotes the heterogeneity of the surface of the adsorbent; this is in agreement with results obtained with the Freundlich model and Redlich–Peterson isotherm model indicating that the surface of the prepared adsorbent was heterogeneous in nature.

IV. CONCLUSION

The present study established the fact that PGD treated with SDS may be efficiently used as an adsorbent for the removal of RV5 from aqueous solutions. The amount of dye adsorbed was found to vary with pH, dye concentration, and contact time. The observed optimal removal of RV5 occurred at a pH of 1-2. Equilibrium time was found to be approximately 30 minutes for 50 mg/l of dye solution for treated and untreated adsorbents in this study. The adsorption of SDS and TX100 treated PGD tightly fitted into pseudo-second-order, power function, and Elovich non-linear kinetic models with significant correlation coefficients. Also, the Intraparticle diffusion model analysis was indicative of a multi-path diffusion mechanism being involved in the adsorption of RV5 by PGD. Furthermore, the Freundlich model and Sips isotherm model showed a strong correlation indicating that the surface of the prepared adsorbent was heterogeneous in nature.

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