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Adsorption, Equilibrium and Kinetic Studies of the Removal of Methyl Violet from Aqueous Solution Using White Potato Peel Powder

C.E. Enenebeaku[1,a], I.C. Ukaga[2,b], J.N. Okorocha[1,c], B.I. Onyeachu[3,d]

[1]Department of Chemistry, Federal University of Technology Owerri, P.M.B 1526, Owerri Imo state, Nigeria

[2]Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State Nigeria

[3]Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

[a]enecon92002@yahoo.com, [b]ikechris2002@yahoo.com, [c]emybeck@yahoo.com, [d]benedictonyeachu@gmail.com

Keywords: Adsorption; Methyl Violet; Freundlich Isotherm Model; Contact Time

Abstract. The adsorption of methyl violet (MV) dye onto white potato peel powder (WPPP) from aqueous solution was investigated by analyzing the operational parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature to observe their effects in the dye adsorption process. The optimum conditions for the adsorption onto the adsorbent (WPPP) was found to be contact time (100 mins), pH (10.0) and temperature (303K) for an initial dye concentration of 50 mg/L and adsorbent dose of 1.0g. The experimental equilibrium adsorption data of the dye fitted best and well to the Freundlich isotherm model. The maximum adsorption capacity was found to be 17.13mg/g for the adsorption. The kinetic data conforms to the pseudo-second order kinetic model.

1. Introduction

Methyl violet is a family of organic compounds that are mainly used as dyes. Dyes are natural or synthetic aromatic compounds which have various functional groups and also have the properties of imparting their colours to other substances [1, 2]. Dyes are one of the major undesirable constituents of the wastewater produced from many industries such as textile, paint, ink, plastics, pulp and paper, cosmetics, tannery etc. (2-6). Textile industries are the largest consumers of dyestuff and most of the dye effluents are discharged directly or indirectly into receiving natural water bodies [4-6]. Most of the effluents are coloured effluents containing different dyestuff such as methyl violet. These coloured dyestuffs reduce the penetration of light into the aquatic environment, causing a significant reduction in the photosynthetic activities of hydrophytes and also maybe toxic to some aquatic organisms due to the recalcitrant nature of the dyes [8, 9]. Methyl violet is a mutagen and mitotic poison. Compounds related to methyl violet are potential carcinogens [3]. In this regards, considering the high environmental pollution and serious health risk factors associated with production and discharge of dye effluents into natural water bodies, national and international agencies has passed strict rules concerning the production and use of these synthetic colorants. There is therefore need to treat industrial effluents containing dyes before discharging them into water bodies. In the present investigation, we conducted the removal of methyl violet from aqueous solution with white potato peel powder as the adsorbent. Methyl violet is a class of triphenylmethane having a molecular formula ($C_{25}H_{30}ClN_3$) [4].

Conventional methods of removal of dyes from waste water effluents include electrochemical techniques, coagulation and flocculation, adsorption, photocatalytic degradation, ozonation [10-14]. Many of the processes mentioned above are not cost effective and hence may not be very suitable for the removal of dye effluents from waste water in developing countries. Adsorption method has recently gained more favour than the other methods of removal of dyes. Adsorption process has simplicity of design, more efficient, easy to operate, insensitive to toxic substances and cost effective. It therefore provides an alternative method to other expensive existing physical/ chemical/ biological methods for the removal of dyes from industrial effluents or waste water [19].

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In recent years there has been increasing interest in the use of low cost agricultural materials as adsorbent for the removal of industrial effluents or waste water over the use of activated carbon. Activated carbon has been generally used as a good adsorbent for the removal of dyes from waste water or aqueous solutions due to its high adsorption capacity; but however, this has been greatly limited by the high cost of production and regeneration in its application for pollution control processes. Quiet a good number of studies for the removal of dyes from aqueous solution have been carried out using low cost agricultural materials as adsorbent [1, 9, 13, 15, 19]. However, research interest into production of more new economical, easily available and highly efficient adsorbents are still under development. For this reason, this study was undertaken to investigate the possibility of the removal of methyl violet from aqueous solutions (dye effluents).

2. Experimental

2.1. Adsorbents collection and Preparation

The white potato peels was collected from Federal University of Technology Owerri market and its environs in Owerri West Local Government Area of Imo State, Nigeria. These white potato peels, (WPP) collected were properly washed with running water to remove sand, dirt and other impurities present in them and is dried in an oven (at 50°C) until all moistures were removed. The dried samples were ground in a mill and sieved using a sieve shaker of particle size 300µm. The samples that passed through the sieve were stored in separate air tight containers and used as adsorbents without any further pretreatment.

2.2. Preparation of Methyl violet Solution

Stock solution of the Methyl violet dye was prepared by dissolving 1g of the powdered dye in 1L distilled water respectively to achieve 1000 mg/L dye concentration in the solutions. Experimental dye solutions of desired concentrations were obtained by appropriate dilution of each stock solution.

2.3. Adsorption studies

Adsorption studies were carried out in 100 mL flasks which are mounted on a rotary shaker at 100 rpm agitation. 1g of the adsorbent (WPPP) was weighed in the set of conical flasks of (250 mL) each. 100 mL of methyl violet solution of concentration 50 mg/L were measured into the different sets of flask properly sealed and agitated separately for 10, 20, 40, 60, 80, 100 and 120 min. to study the effect of contact time and to obtain an optimum contact time for which all other experiments were agitated. Using the same amount of methyl violet solution and adsorbent dosage of 1g, the effect of temperature was studied at 30, 40, 50, 60 and 70 ^{o}C; while the effect of pH was studied for pH 2, 4, 6, 8 and 10 (obtained by introducing 0.1 M HCl or NaOH solution into the dye solution and measuring with a DEEP VERSION model (EI) pH meter (2). The effect of initial dye concentration on the adsorption of methyl violet onto the adsorbent were studied at pH 7 , by varying the methyl violet solution concentration as 25, 50, 75, 100 and 125 mg/L. The effect of adsorbent dosage on the adsorption of methyl violet was studied with 0.5, 1, 2, 3 and 4 g of WPPP for methyl violet concentration of 50 mg/L at pH 7. At the end of each experiment, the samples were withdrawn from the flasks, centrifuged and filtered. Thereafter, the concentration in the supernatant solution was analyzed using UV-visible Spectrophotometer. The adsorption capacity of the methyl violet dye was calculated using the following general formula: [18-20]

$$qe = \frac{(Co - Ct)V}{W} \quad , \tag{1}$$

where q_e is the amount of methyl violet adsorbed at equilibrium per unit weight of adsorbent (mg/g), Co and Ct (mg/L) are the dye concentrations in the solution before and after adsorption, V is the solution volume (in liter (L), and W is the amount of adsorbent (in gram) used in the adsorption experiment.

The dye percent removal (%) was calculated using the following equation:

$$\% \text{ Dye removal} = \frac{Co - Ct}{Co} \times 100 \quad . \tag{2}$$

3. Results and Discussion

3.1. Effect of contact time:

Fig.1 represents the plot of the effect of contact time on the adsorption capacity and percentage removal of methyl violet by WPPP. It is observed that there is a steady rise in the sorption of methyl violet dye by WPPP until the optimum adsorption (equilibrium time) at 100 minutes. It can be inferred from the rapid sorption that there are abundance of active sites on the external surface of WPPP which resulted in the rapid dye removal from the solution [21].

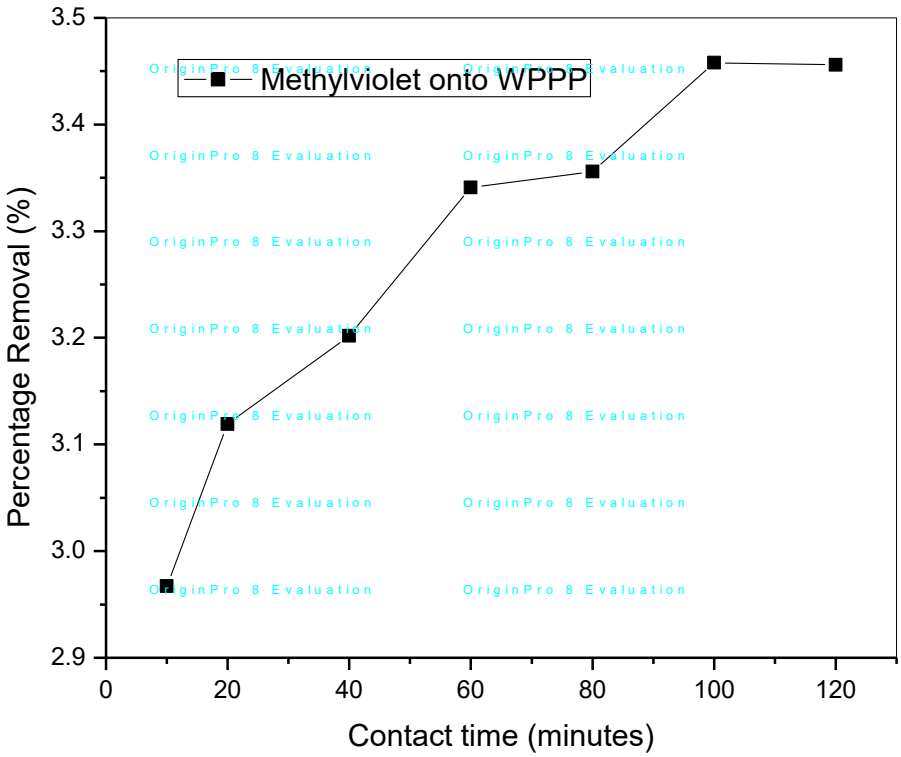

Figure 1. Effect of contact time on percentage removal

3.2. Effect of adsorbent dosage:

The results obtained for the effect of adsorbent dosage on the adsorption of methyl violet are shown in Fig. 2. The study of the effect of adsorbent dosage on methyl violet was carried out with a dye concentration of 50 mg/L at different adsorbent dosages (0.5-4) g, and at a fixed agitation speed (100 rpm) at a contact time of optimum adsorption (100 min). The percentage removal of methyl violet dye from the plot increased from 33.02 % to 60.65%. While the adsorption capacity of the dye decreased from 3.30 to 0.7 mg/g as the dosage increased from 0.5 to 4g. It is observed from the plot that there is a sharp increase in the percentage removal of the dye as the dosage increase from 0.5 to 1 mg/g which thereafter nearly remained constant. The decrease in adsorption capacity with increase in adsorbent dose may mainly be attributed to the non- saturation of the adsorption sites during the adsorption process [22]. The increase in percentage removal of the dye with increase in adsorbent dose maybe attributed to increased adsorption surface area and availability of more adsorption sites which increases with increase in adsorbent dose [23-24].

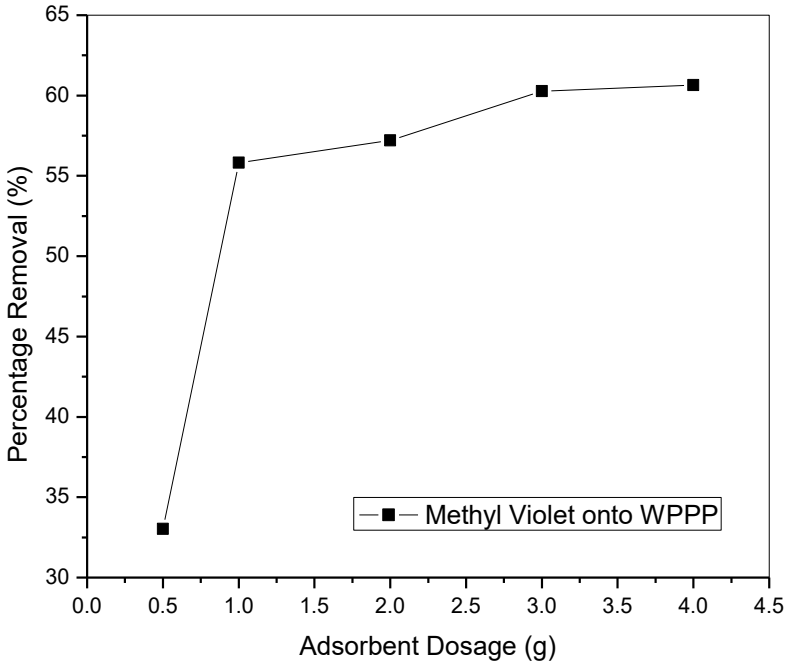

Figure 2. Effect of adsorption dosage on the percent removal of methyl violet by WPPP

3.3. Effect of Initial concentration of Methyl violet

Fig. 3 shows the variation of amount of methyl violet dye adsorbed, q_e, for different initial dye concentration in the presence of 1 g WPPP adsorbent after 120 min. contact time at 27 ^oC. The result clearly shows that the amount of dye adsorbed (q_e) steadily increased from 2.228 mg/g in the presence of 25 mg/L of methyl violet to a maximum of 10.226 mg/g in the presence of 125 mg/L of methyl violet. Such trend has also been reported for the adsorption of many dyes on several other adsorbents [25, 26].

The percentage dye removal of the methyl violet is plotted against the initial dye concentration as show in Fig 4. It is observed that the adsorption capacity of dye increased from 2.23 to 10.23 mg/g. While the percentage removal of the dye decreased from 91.56 to 54.51% as initial concentration increased from 25 to 125mg/L. The increase in adsorption capacity with increase in initial concentration is due to the high driving force which overcomes the mass transfer resistance at higher initial dye concentration [2, 27]. The decrease in percentage removal with increase in dye concentration maybe attributed to the fact that, a given mass of adsorbent has a specific or fixed amount of dye it can absorb. Thus, this may simply be because the adsorbent has reached its peak adsorbent capacity.

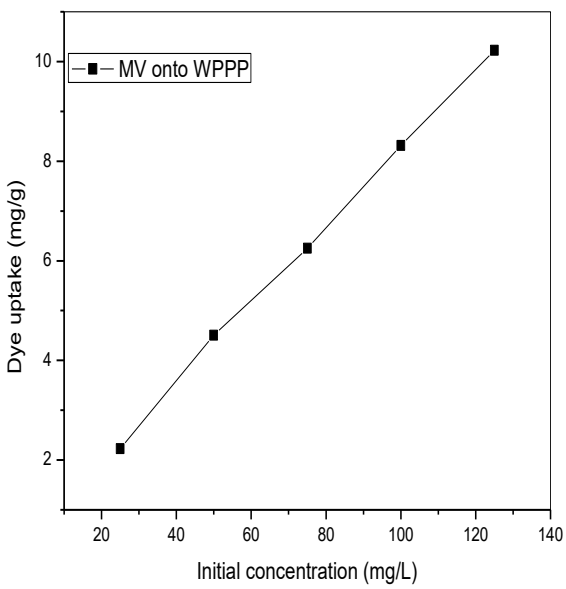

Figure 3. Effect of initial concentration on the dye uptake of MV by WPPP

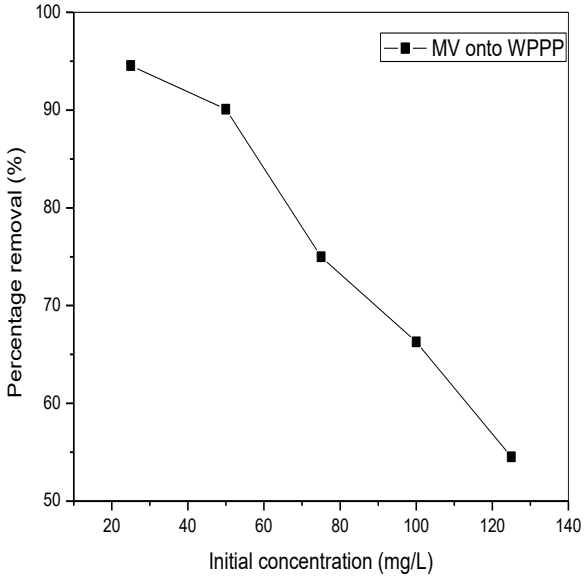

Figure 4. Effect of initial concentration on the percentage removal of MV by WPPP

3.4. Effect of temperature

In the presence of 1 g of WPPP adsorbent and 100 mL of 50 mg/L of methyl violet solution, the variation in the amount of Methyl violet dye adsorbed per unit mass of the WPPP adsorbent, q_e, and the percentage removal of methyl violet for temperature varying between 30 - 70 are as shown in Figs. 5 and 6. By increasing the temperature, the q_e values continuously increased. The percentage removal and adsorption capacity decreased from 80.65% to 75.95% and 4.03mg/g to 3.85mg/g respectively as the temperature increased from 30 t0 70^0 C. This decrease in adsorption capacity and efficiency with increase in temperature maybe attributed to mainly the fact that the physical bonding between the dye (adsorbate) and the active sites of the adsorbent is weakened as the temperature rises. In addition, the dye solubility increases also, causing the interaction between the solute and solvent to become stronger than that between solute and adsorbent. This therefore, makes it more difficult for the solute to adsorb [27].

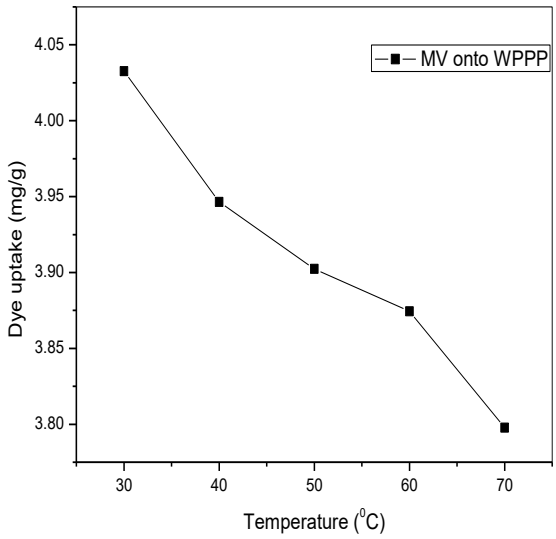

Figure 5. Effect of temperature on the adsorption capacity of MV onto WPPP

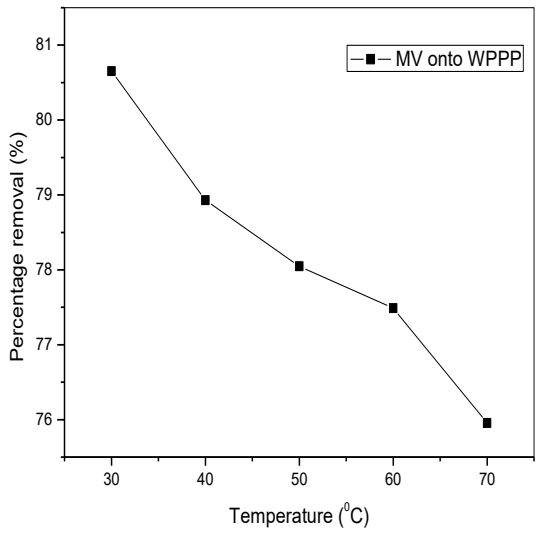

Figure 6. Effect of temperature on the percentage removal of MV by WPPP

3.5. Effect of pH

The effect of pH on the adsorption capacity and percentage removal of methyl violet onto WPPP was studied using 1 g of WPPP adsorbent and 100 mL of 50 mg/L of methyl violet dye solution with different pH values (2-10). 100ml of each of the solution was added to 1g of the adsorbent and agitated at the contact time of optimum adsorption at room temperature.

The results of the effect of solution pH on methyl violet dye adsorption are as illustrated in Fig. 7 and Fig. 8. From Fig. 7 it is seen that the values of the adsorption capacity increased from 3.89 mg/g to 4.42 mg/g as the pH varied from 2–10. Fig. 8 also shows that the percentage removal of the methyl violet dye by the WPPP increased from 77.86% to 82.9% as pH increases from 2 to 10. The optimum sorption was found at pH 10. The increase in percentage removal and adsorption capacity with increase in pH maybe attributed to the fact that at low pH values of the solution, the presence of excess hydrogen ion (H^+) in the solution competes with the cationic groups of the methyl violet dye for the adsorption sites on the adsorbent surface. While at high pH values, the positive charges (H^+) at the solution interphase decreases and the adsorbent surface is more negatively charged, thus enhancing attraction of more amounts of the anions of the methyl violet dye [12].

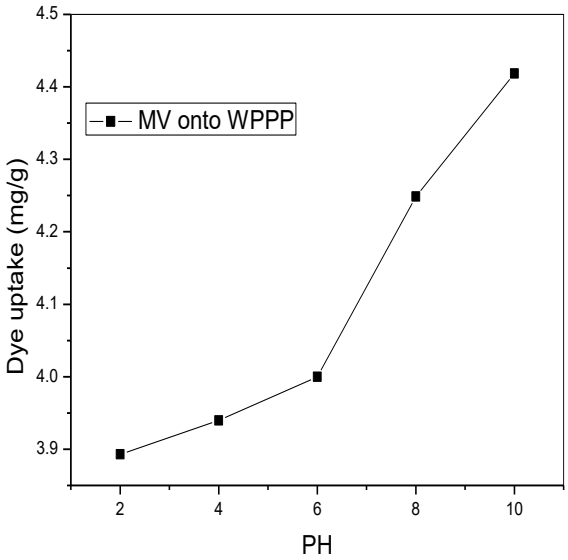

Figure 7. Effect of PH on the adsorption capacity of MV

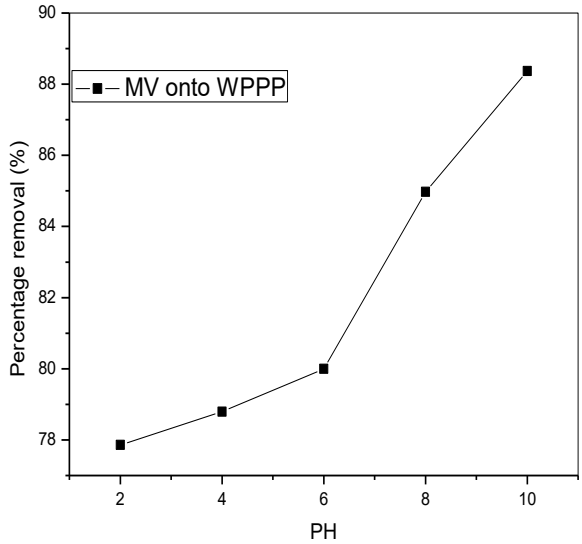

Figure 8. Effect of PH on the percentage removal of MV by WPP

3.6. Adsorption Equilibrium Study

The Langmuir and Freundlich models were adopted to analyze the adsorption data obtained for the adsorption of methyl violet onto WPPP. The adsorption isotherm is the relationship between the amount of a substance adsorbed at a constant temperature and its concentration in the equilibrium solution [28]. Equilibrium adsorption isotherm equations are used to analyze the experimental adsorption data. The parameters derived from the Langmuir and Freundlich models are important in providing information on the adsorption mechanism, surface characteristics and affinities of the adsorbent [28].

The linearized forms of the Langmuir and Freundlich isotherms are used to analyze the experimental data obtained to have a better understanding of the nature of the interaction between the adsorbent WPPP and the methyl violet dye.

The linearized form of the Langmuir isotherm equation is as show in equation 3 below:

$$\frac{Ce}{qe} = \frac{i}{b}\left(\frac{1}{qm}\right) + \frac{Ce}{qm} \ , \tag{3}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of the dye adsorbed at equilibrium (mg/g) and q_m and *b* are Langmuir constants which are related, respectively, to the adsorption efficiency and adsorption energy. A plot of C_e/q_e against C_e for the Langmuir isotherm is as shown in Fig. 9, where $1/q_m$ and $1/(bq_m)$ are the slope and intercept respectively. The values of q_m and *b* were calculated from the slope and intercept of the plot, and their values (with correlation coefficient, R^2) are as shown in the Table 1.

The Freundlich isotherm model is an empirical equation that can be used for non ideal sorption involving a heterogeneous adsorption (28). The linear form of the equation is given below:

$$Log\ qe = Log\ K + \frac{1}{n} Log\ Ce \ , \tag{4}$$

where q_e is the amount of dye adsorbed at equilibrium, C_e is the concentration of the dye solution at equilibrium (adsorption capacity) 1/n is a constant (representing adsorption intensity). The plot of Log q_e versus Log C_e is a straight line graph as shown in Fig. 10. Log K and 1/n are the intercept and slope respectively. The values of K and 1/n, given in Table 1, were calculated from the intercept and slope respectively of the plot.

The Langmuir and Freundlich isotherm constants are presented in Table 1. From this Table, it can be seen that the regression correlation coefficient (R^2) of the Freundlich equation (R^2 = 0.95) is more linear when compared with that of the Langmuir equation (R^2 = 0.887) implying that the adsorption isotherm data are well fitted by the Freundlich isotherm. The fact that the Freundlich isotherm fits the experimental data very well may be due to the heterogeneity of the surface of the WPPP adsorbent because application of the Freundlich equation involves the assumption that the surface is heterogeneous.

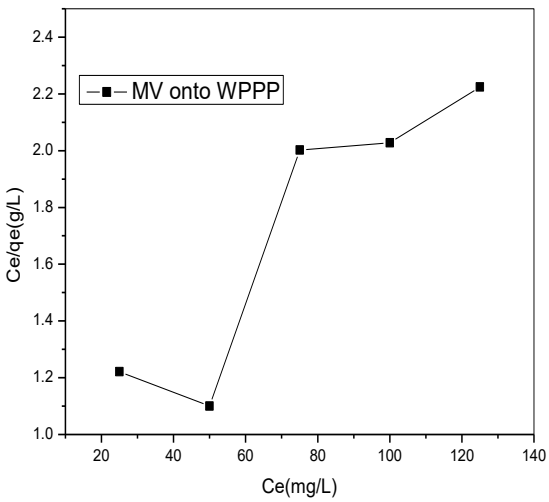

Figure 9. Langmuir plot for adsorption of MV onto WPPP

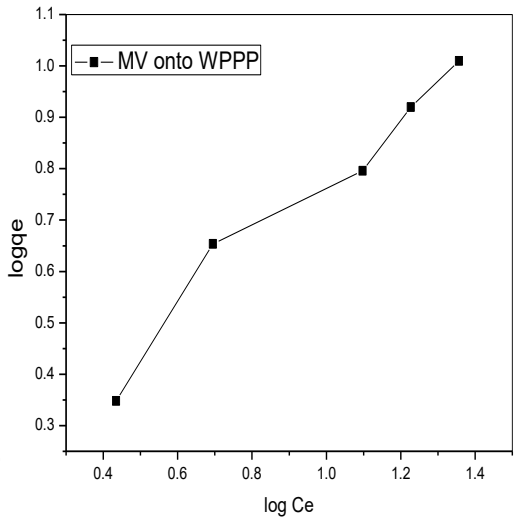

Figure 10. Freundlich plot for adsorption of MV onto WPPP

Table 1. Langmuir and Freudlich isotherm parameters for the adsorption of Methyl violet onto WPPP at 25 ºC

Langmuir			Freundlich		
qm (mg/g)	b	R2	n	Kf (mg/g) (L/mg)1/n	R2
17.13	1.0	0.887	1.517	1.291	0.95

3.7. Adsorption Kinetics

The adsorption kinetics of the adsorption of methyl violet dye was studied using the pseudo-first order and pseudo-second order kinetics model. These models enable the computation of the extent of dye uptake in the adsorption process.

The linear form of the pseudo –first order kinetic model is represented by the following equation:

$$In(qe - qt) = Inqe - Kt \ , \tag{5}$$

where *qe* and *qt* are the values of amount of the dye adsorbed per unite mass on the adsorbent at equilibrium and at various time t, respectively. K_1 is the pseudo-first order adsorption rate constant (min^{-1}). The values of K_1 and the calculated qe are determined from the slope and intercept respectively of the linear plot of $In(qe - qt)$ versus t.

The pseudo-second order kinetic model is expressed by as:

$$\frac{t}{q_t} = \frac{1}{K_2 q^2} + \frac{1}{q_e} t \ , \tag{6}$$

where K_2 is the pseudo-second order adsorption rate constant (g/mg/min) and q_e is the amount of dye adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate h ($mg.g^{-1}. Min^{-1}$) is expressed as:

$$h = K_2\ q^2\ \ . \tag{7}$$

The plot of t/q_t versus t gives a linear relationship which allows computation of K_2, h and calculated q_e.

The applicability of these models is based on the judgment on the respective correlation coefficient (R^2) and the agreement between the experimental and calculated value of q_e

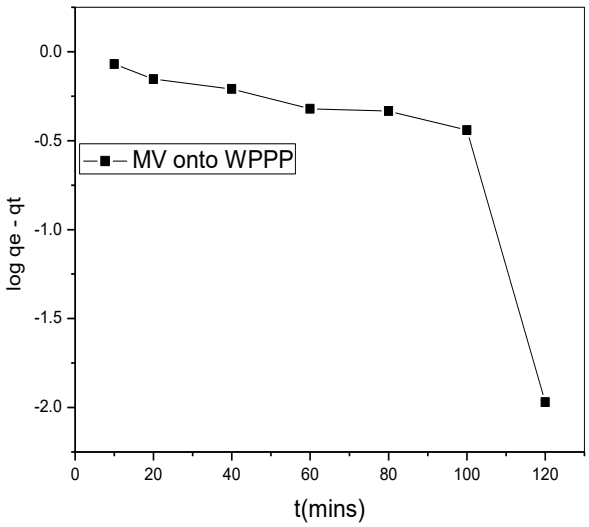

Figure 11. Pseudo-First order plot for Adsorption of MV onto WPPP

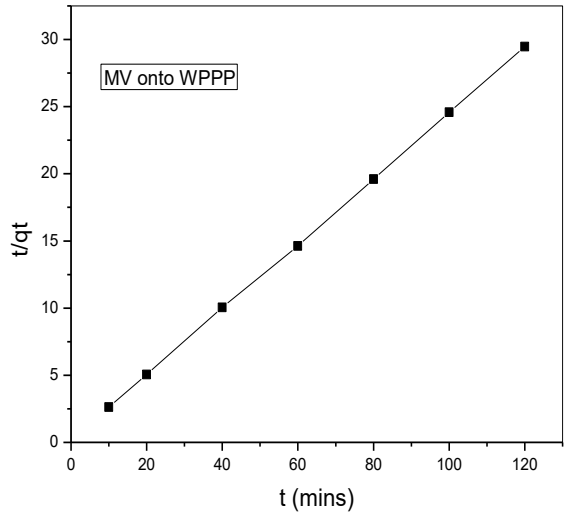

Figure 12. Pseudo-First order plot for Adsorption of MV onto WPPP

Table 2. Pseudo-first order and second order kinetic model parameters

Pseudo–first Order Model				Pseudo–second Order Model			
qe (exp)	k1 ($g.mg^{-1}\ min^{-1}$)	qe (cal) (mg/g)	R^2	H ($mg.g^{-1}\ min^{-1}$)	k_2 ($g.mg^{-1}\ min^{-1}$)	qe (cal) (mg/g)	R^2
3.82	0.028	1.795	0.497	0.659	0.046	3.776	0.989

Figs. 11 and 12 depict the pseudo–first order and second order kinetics for the adsorption of Methyl violet by WPPP respectively. The pseudo-second order rate constants K_2, and q_e determined from the model, as well as the correlation coefficient are presented in Table 2. It is observed from Table 2 and Fig. 12 that there is good agreement between the calculated q_e values and the experimental q_e values i.e. q_e (cal.) and q_e (expt.). Table 2 also reveals a very high correlation value (R^2= 0.989) for the adsorption of methyl violet by WPPP. The pseudo-first order rate constant (K_1) and q_e determined from the model as well as the correlation coefficient of the plot are presented in Table 2. and Fig.11. It is observed from Table 2 that the relationship between the dye diffusivity, In (q_e – q_t) and time t, is non – linear with a low correlation coefficient (R^2 =0.497). It is also observed that the calculated q_e values did not agree with the experimental q_e since the calculated q_e values were neither equal nor reasonably close to the experimental q_e values (Table 2). This therefore, leads to the conclusion that the pseudo-first order model was inadequate in representing the adsorption of methyl violet onto WPPP. It is therefore evident that the pseudo-second order model is the best fit kinetic model in describing the adsorption processes of methyl violet onto WPPP.

3.8 Adsorbent characterization

FTIR spectral of WPPP before and after adsorption as shown in Fig 13 and 14 of MV dye were scrutinized to monitor the shifting mechanism of the functional groups existing in the adsorbent. For WPPP before adsorption, various peaks are at 3421.13cm^{-1}(O-H stretch, H-bonded), 2932 cm^{-1} (C-H stretch from alkane), 1716.94 cm^{-1} and 1734.10 cm^{-1}(C=O stretch), 1653.61 cm^{-1} (C=C stretch),

1521.90 cm^{-1} and 1534.06 cm^{-1}(N-O asymmetric stretch), 1457.31 cm^{-1} (C-H bend), 1418.95 cm^{-1} (CH3), 1154.94 cm^{-1} (C-N stretch), 1023.28 cm^{-1} (C-O stretch), 930.01 cm^{-1}(O-H bend from carboxylic acid), 860.83 cm^{-1} (C-Cl stretch) and 526.16 cm^{-1} (C-Br) [29]. After adsorption of MV dyes it was found out that most of the functional groups were affected after the uptake process. This is judged from shifts in the position of some of the functional groups to lower or higher band intensity after MV adsorption. The functional groups that moved to lower band intensity includes: C-H from 2932 – 2931.49 cm^{-1}, C=O from 1716.94 and 1734.10 cm^{-1} to 17.1673 and 1733.86 cm^{-1} respectively, C=C from 1653.61 to 1647.20 cm^{-1}, N-O from 1521.90 and 1534.06 cm^{-1} to 1507.48 and 1521.76 cm^{-1} respectively, C-O from 1023.28 to 1019.19 cm^{-1}. The functional groups that moved to higher band intensity includes: O-H from 3421.13 to 3447.07 cm^{-1}, C-Cl from 860.83 to 861.11 cm^{-1}. This indicates involvement of these groups for MV binding to WPPP [30].

Fig. 15 shows the SEM image of WPPP powder. It can be observed (from Fig. 15) that the external surface of WPPP powder is very irregular with rough edges and presence of few pores.

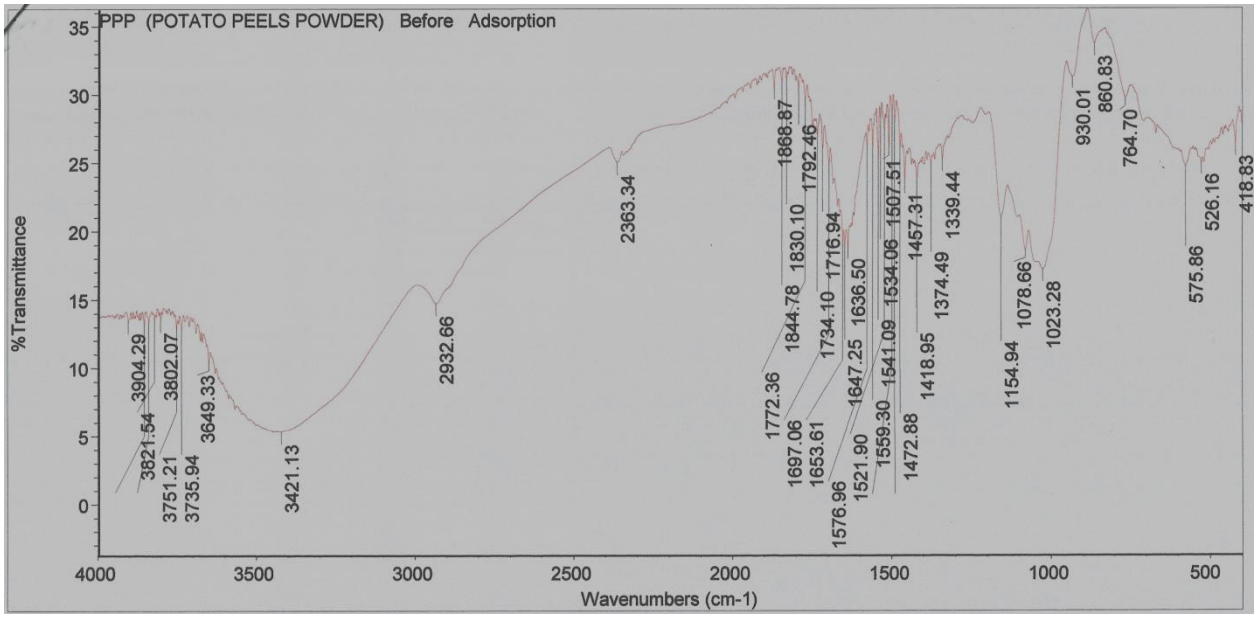

Figure 13. FTIR spectra of WPPP before adsorption.

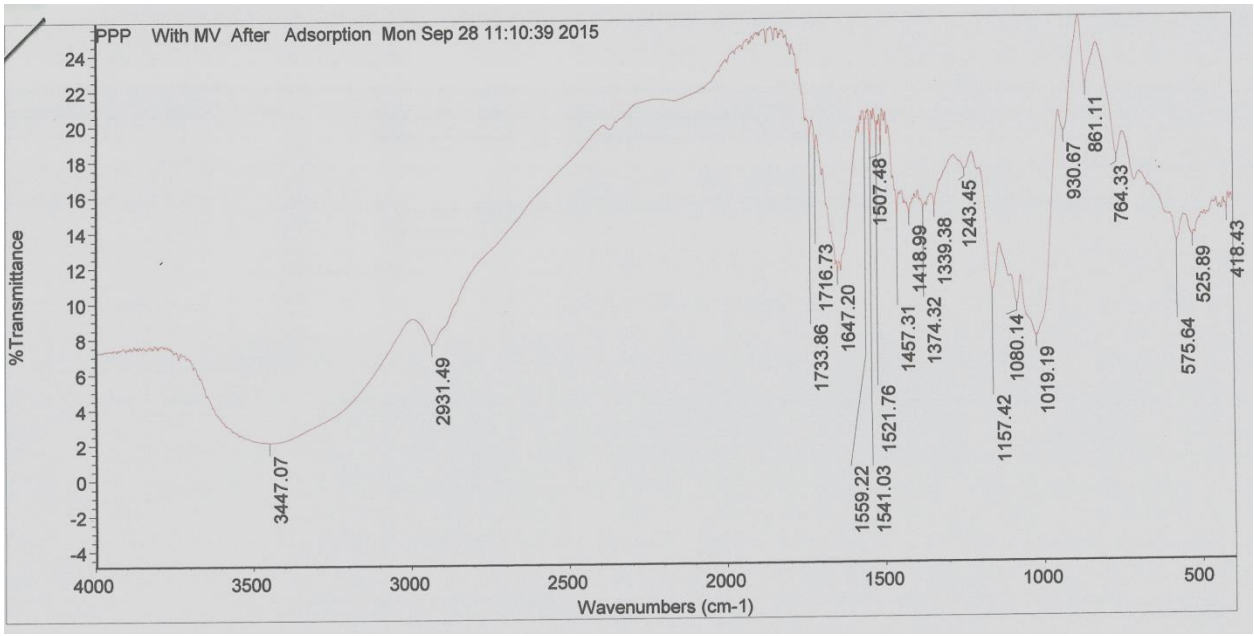

Figure 14. FTIR spectra of WPPP after adsorption of MV

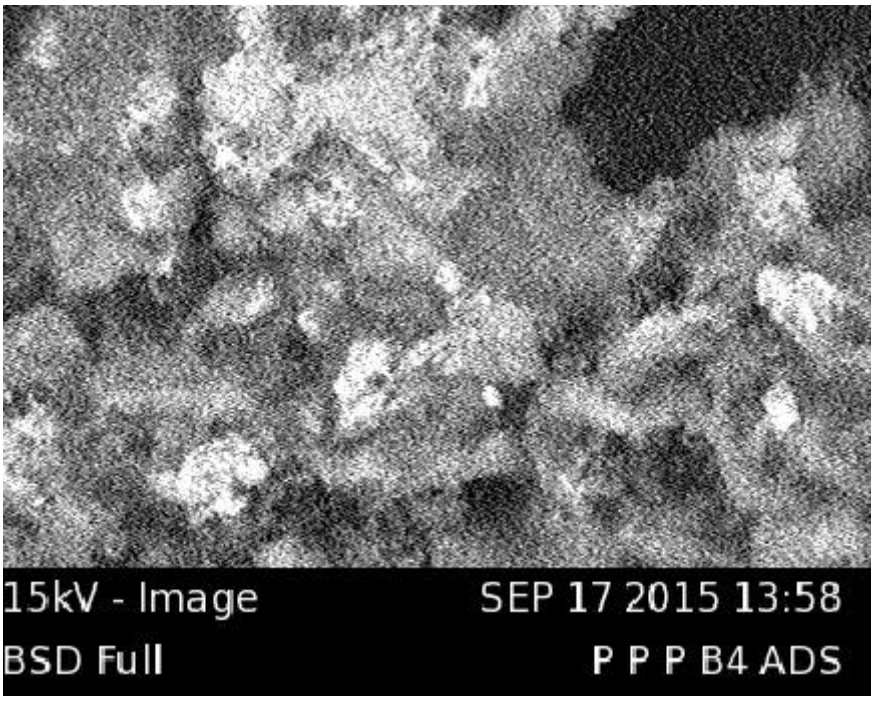

Figure 15. SEM image of WPPP powder at 2500x

Conclusion

White potato peels (WPP) powder has been identified as an effective adsorbent with a high potential for the removal of methyl violet dye from aqueous medium. The removal of methyl violet dye by WPPP from aqueous medium was found to be influenced by contact time, adsorbent dose, initial concentration, temperature and initial pH of solution. The optimum adsorption of methyl violet dye by WPPP was found at pH 10. Increasing contact time increased the amount of Methyl violet dye adsorbed up to an optimum value. Temperature had strong influence on the adsorption processes and maximum dye uptake was 303K. Increasing initial dye concentration, temperature and pH led to increasing amount of methyl violet adsorbed onto the WPPP adsorbent. The kinetic studies showed that the adsorption of methyl violet dyes onto WPPP adsorbent followed the pseudo-second order kinetic model. The study on equilibrium sorption revealed that the Freundlich isotherm model gave the best fit to the experimental data.

Conflict of Interest

The authors declare that there is no conflict of interest.

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