OPTIMIZATION OF ADSORPTION OF 5-AMINO-4-HYDROXY-3-[(E)-(5-NITRO-2- THIENYL)DIAZENYL]-2,7-NAPHTHA-LENEDISULFONIC ACID MONO SODIUM FROM AQUEOUS SOLUTION USING ACTIVATED *TELFAIRIA OCCIDENTALIS* SEED WASTE

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Abstract

The potential of activated carbon, prepared from fluted pumpkin seed waste for the adsorption of an azo dye: 5-amino-4-hydroxy-3-[(E)-(5-nitro-2-thienyl)diazenyl]-2,7-naphthalenedisulfonic acid mono sodium, from aqueous solution was investigated. Chemical activation method was adopted for the preparation of the adsorbent, using $ZnCl_2$ as the activating agent. The adsorbent prepared was characterized on the basis of activated carbon yield, ash content, iodine sorption capacity and surface area. The activated carbon yield was found to be 50.40%; ash content was 0.18%, iodine sorption capacity of 92.68% and a surface area of 625.00 m^2/g. The effect of pH, adsorbent dose, initial dye concentration and contact time on removal efficiency of the dye by the adsorbent was studied. Full factorial design (FFD) of experiment was employed to optimize the adsorption process. The result obtained indicated that the optimum condition of pH 5.00, adsorbent dose of 0.10 g, initial dye concentration of 5.00 ppm and contact time of 20.00 minutes, gave 99.50% removal efficiency. This value obtained falls within the recommended value of ≥80% for good adsorbents. The experimental removal efficiency value of 99.50% observed was in good agreement with the value predicted of 99.94% by the FFD.

Introduction

Azo dyes are synthetic colours that contain an azo group, -N=N- as part of the structure. They are used mostly in textile industries. They are common contaminants in waste-water generated from pesticides, paper, textile, petrochemicals and dye manufacturing industries. They are harmful to organisms and also have the potential of being harmful to human health. Due to the risk posed by the presence of this dye in water bodies, various methods have been employed for their removal from waste water treatment, including adsorptive treatment using activated carbon. Various agricultural by-prod-

ucts have been reported to be capable of been converted to activated carbon (Bhatnagar & Sillanpaa, 2010; Ioannidou & Zabaniotou, 2007). There is a growing interest in cost innovative material that will be useful in the treatment of waste-water.

Telfairia occidentalis (TEL) is a creeping vegetative shrub which is grown in East Africa, mainly for its oil and protein-rich seeds; it is also grown in West Africa for its nutritious leaves and seeds (Okoli & Nyanayo, 1988). It is commonly called fluted pumpkin. Many studies have been reported on the proximate composition and nutritive values of leaves and

seeds of this plant (Fasuyi, 2008; Effiong *et al.*, 2009). The nutritional value of this vegetable makes it the largest consumed vegetable in West African sub-region. Oil is also generated from the seed and the seed waste creates one of the major agro waste problems in Nigeria. Several studies reports on the conversion of the seed shell and stem waste of this plant into activated carbon (Ekpete *et al.*, 2011; Verla *et al* 2012), but there are no reports on the potential of using its seed waste for the production of activated carbon. Adsorption process is influenced by factors such as adsorbent dose, initial dye concentration, contact time and pH. The effect of these factors on the adsorption efficiency of the prepared activated carbon was studied using Full Factorial Design technique, which is an analytical tool that makes it possible to detect the frequent interactions which occurs between two or more factors. The evaluation of the best adsorption conditions of materials in different medium have been made by several researchers by using Full Factorial Design technique (Kavak, 2009; An *et al.*, 2012). Hence, this research is aimed at exploiting the possibility of producing adsorbent from fluted pumpkin seed waste and studying its efficiency for removing an azo dye from aqueous system.

Experimental

Sample collection and preparation
The seed waste obtained from the extraction of oil from the seeds of *Telfairia occidentalis* was oven dried at 105°C and crushed with laboratory mortar and pestle. The resulting particles were sieved (using a manual sieve) to obtain particle sizes of 3.00 μm and then kept for further analysis.

The activation method adopted for this work is chemical activation using zinc chloride salt ($ZnCl_2$) as the activating agent. 10.00 g of the raw material was impregnated with $10.00 cm^3$ of 30% $ZnCl_2$ for a period of two hours to obtain a ratio of 1:1. The impregnated material was then activated at 400°C for one hour. The adsorbent (TZAC) was then washed with distilled water, dried at 105°C and kept for characterization.

Ash content determination
The prepared adsorbent (10.00 g) was placed into a porcelain crucible and weighed (W_i). This was then placed in a preheated furnace set at a temperature of 900°C. The crucible was left on for one hour after which it was transferred into desiccator and allowed to cool. The crucible and content was then re-weighed (W_f). The percentage ash content (on dry basis) is given by:

$$(W_i - W_f)/W_i \times 100$$

where: W_i is the initial weight of crucible with sample.

W_f is final weight of crucible with sample.

Surface area determination
The particle bulk density was determined using the procedure of Ahmedna (1997) as follows: An empty measuring cylinder of $50.00 \ cm^3$ capacity was weighed and the weight noted (W_c). The cylinder was then filled with a sample of activated carbon from the seeds and gently tapped until there was no more change in the level of the sample in the measuring cylinder. The weight of the cylinder plus the packed sample was noted (W_c). The weight of the packed sample ($W_s = W - W_c$) was then calculated and recorded .

Then, Bulk Density $(B_d) = W_s/V_s$

Where: V_s is the volume occupied by the packed sample.

The surface area was determined using the relation:

$SA = 6(cm^2/g)/ B_d P_d$ (Kwaghger & Adejor, 2012)

P_d = particle size (particle diameter)

Activated carbon yield
Dried weight, W_c of each carbon sample was determined and the activated carbon (AC) yield was calculated as follows;

$$Carbon\ yield\ (\%) = \frac{W_c}{W_0}\ x100\%$$

Where: W_c is the dry weight (g) of the final activated carbon and

W_0 is the dry weight (g) of the precursor.

Iodine sorption capacity
Iodine sorption capacity of the prepared adsorbent was determined as follows. Exactly 1.00 g each of the AC sample was weighed into a 250 cm³ flask and 10.00 cm³ of 5% HCl was added. The flask was swirled until the carbon became wet. Iodine solution (2.70 g of iodine and 4.10 g of potassium iodide in one litre of de-ionized water) of 100.00 cm³ volume was added and the mixture was shaken for 5 minutes. All the samples were filtered using Whatman No.1 filter paper. The filtrate (50.00 cm³) was titrated with 0.1M sodium thiosulphate until the solution became pale yellow. Then 1.00 cm³ of starch indicator solution (1%) was added and the titration was continued with sodium thiosulphate until the solution became colourless. A blank was prepared without adding AC and titrated similarly. The % iodine sorption by each AC sample was calculated by applying the following formula:

$$Iodine\ sorption\ capacity\ (\%) = \frac{V_{sb}-V_{sb}}{V_{sb}}\ x100$$

Where: Vsb is the volume of sodium thiosulphate used for blank and Vss is the volume of thiosulphate used for sample.

Scanning Electron Microscopy
The texture and pore structure of the activated carbon prepared was examined under a Scanning Electron Microscope (SEM) at different magnifications.

Fourier Transform Infrared (FTIR) analysis
Functional groups were determined using FTIR by preparing KBR pellet of material.The azo dye used in this work, 5-amino-4-hydroxy-3-[(E)-(5-nitro-2-thienyl)diazenyl]-2,7-naphthalenedisulfonic acid mono sodium (Fig. 1), was synthesized in our previous research (Iyun *et al.*, 2012). The dye was chosen to ensure that after dyeing residue can be taken care of, so as not to constitute health hazard to the environment. It is dark purple, water – soluble powder. Its molecular weight is 519 g/mol. Solution of this dye was prepared by dissolving required quantity of the dye in distilled water. All other chemicals ($ZnCl_2$, NaOH and HCl) used for this research were of analytical grades and needed no further purification.
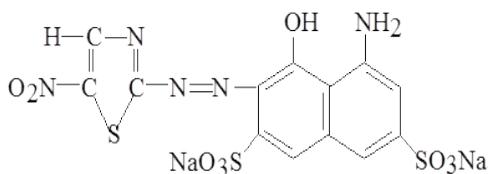
Fig. 1: The chemical structure of 5-amino-4-hydroxy-3-[(E)-(5-nitro-2-thienyl)diazenyl]-2,7-naphthalenedisulfonic acid mono sodium (TD1).

Adsorption Studies
In order to optimize the adsorption processes, four factors which are important variables in adsorption process were selected to study the adsorption of TD1 from aqueous solution by the prepared adsorbent. The variables are; pH (A), adsorbent dosage (B), initial dye concentration (C), and contact time (D). The adsorption process was studied by varying these factors at 2 level factorial approach as shown in Table 1

TABLE 1
Factors and their levels for adsorption studies

Factors	Factor Levels	
	Low level(-1)	High level(+)
pH	5.00	10.00
Adsorbent dosage (g)	00.05	00.10
Initial dye. Conc. (ppm)	1.00	5.00
Contact time(mins.)	20.00	60.00

Batch adsorption study
Stock solution of TD1 dye was prepared in a 1000.00 cm3 volumetric flask by dissolving 1.00 g of the dye in small amount of deionized water in two different flasks and made up to the mark. Working standard solutions of the dye were prepared by diluting the stock solution to obtain concentrations specified by the 24 factorial experimental design for TD1 (Table 1). The pH of the solutions was adjusted using dilute hydrochloric acid and sodium hydroxide solutions as necessary. The experiment was performed at ambient temperature (298K) according to the design generated by the Design-Expert software version 6.0.6 (Stat-Ease Inc., Minneapolis, USA) for the adsorption of the dye. The concentration of dye in the solution at equilibrium was determined (with the aid of a standard calibration curve) by taking absorbance reading on a UV/visible spectrophotometer at 550 nm (the λmax of TD1). Removal efficiency of each dye was then calculated using the equation below.

$$\text{Removal efficiency (\%)} = \frac{c_i - c_f}{c_i} \times 100$$

Where, C_i is the initial concentration of dye solution. C_f is the final concentration at equilibrium.

Results and Discussion
The ash content, carbon yield, surface area and iodine sorption capacity of the activated adsorbent are summarize in Table 2. The carbon yield of 50.40% obtained for the prepared adsorbent is higher than the value reported for adsorbents prepared from other materials (Olafadehan *et al*., 2012). This is an indication that TEL seed waste is a lignocellulosic material with the potential of being converted to activated carbon with good yield.

TABLE 2
Characteristics of the prepared adsorbent

Characteristics	
Ash content (%)	0.18 ± 0.01
Carbon yield (%)	50.40 ± 0.27
Surface area (m^2/g)	625.00 ± 1.29
Iodine sorption capacity (%)	92.68 ± 0.15

Results are given as Mean ± SD (Triplicate measurement)

Ash content refers to a non-carbon or mineral additives that do not combine chemically with the carbon surface. It is the residue that remains when the carbonaceous portion is burnt off. High ash content is undesirable for activated carbon since it has the potential of reducing the mechanical strength of carbon, hence affecting its adsorptive capacity i.e. the overall activity of the adsorbent, as well as the efficiency of reactivation is reduced. The lower the ash value therefore, the better the activated carbon for use as adsorbent. The ash content of the prepared adsorbent was 0.18% which falls within the range 0.1%-15.8% reported for other adsorbents by other researchers (Metcalf & Eddy, 2003; Olafadehan *et al*., 2012; Anisuzzaman *et al*., 2015). The surface area of the activated carbon was 625.00 m^2/gm^2. This value falls within the range of 500-1400 m^2/gm^2 set for good adsorbents (Lartey *et al*., 1999). The prepared adsorbents had surface areas comparable to other adsorbents reported to be of good adsorptive qualities, an indication that the prepared adsorbent is characterized by both micro and meso porosity. The iodine sorption capacity of adsorbents is also related to their micro and meso porosity (Shrestha *et al*., 2012). The iodine sorption capacity of the prepared adsorbent was 92.68%. This high iodine sorption capacity further supports the availability of large surface area for the prepared adsorbent.. The Scanning Electron Micrograph (SEM) images of the untreated sample alongside the carbonized sample are as shown in Fig. 2a and 2b respectively. These figures give an idea of the difference in porosity of the material before and after activation. The SEM image of the raw sample in Fig. 2a shows that the pores in the raw sample are very low and

undeveloped. Fig. 2b shows the SEM image of the activated carbon produced, comparing Fig. 2a with 2b, one can notice that pores in Fig. 2b are better developed than in Fig. 2a. Fig. 3a and 3b show the spectrum obtained for the raw sample and prepared adsorbent respectively. The band width of 3000-2800 cm^{-1} represent C-H stretching in alkane groups. Peaks observed within the width of 1680-1750 cm^{-1} corresponds to C=O stretching vibration in carbonyls, such as ketones, aldehydes, lactones and carboxylic groups (Budinova *et al*., 2006). Band width of 3400-3200 cm^{-1} may be assigned to C-H in alkene, while peaks observed at 1651.12 cm^{-1} may be assigned to the C=C stretching vibration while peaks located at band width of 2300-2375 cm^{-1} may be assigned to C≡C stretching vibrations in alkyne groups (Shaarani and Hameed, 2011). Peaks observed in the region of 1200-1000 cm^{-1} represent C-O stretching vibration of functional groups such as alcohols, esters, carboxylic and esters groups (Tan *et al*., 2007).
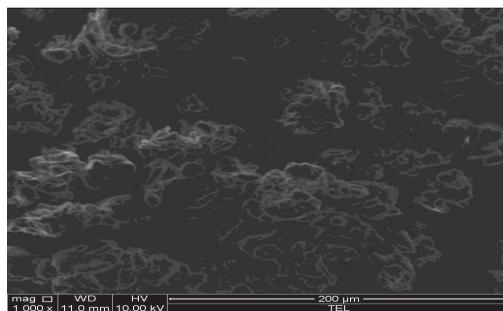

Fig. 2a: Scanning Electron Micrograph of untreated sample.
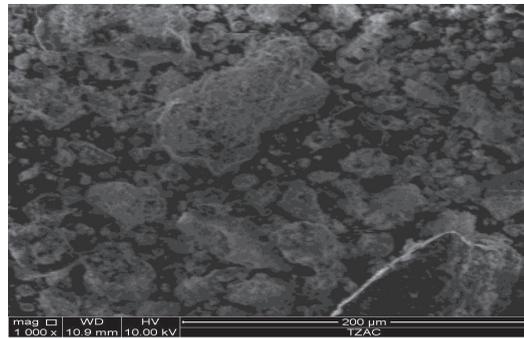
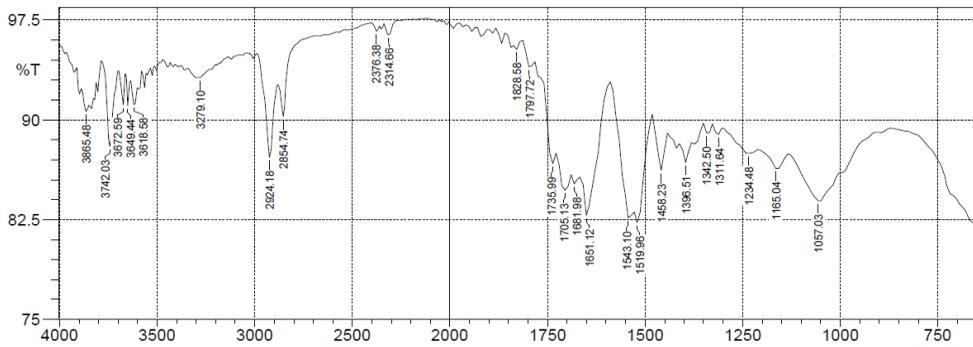Fig. 2b: Scanning Electron Micrograph of prepared adsorbent

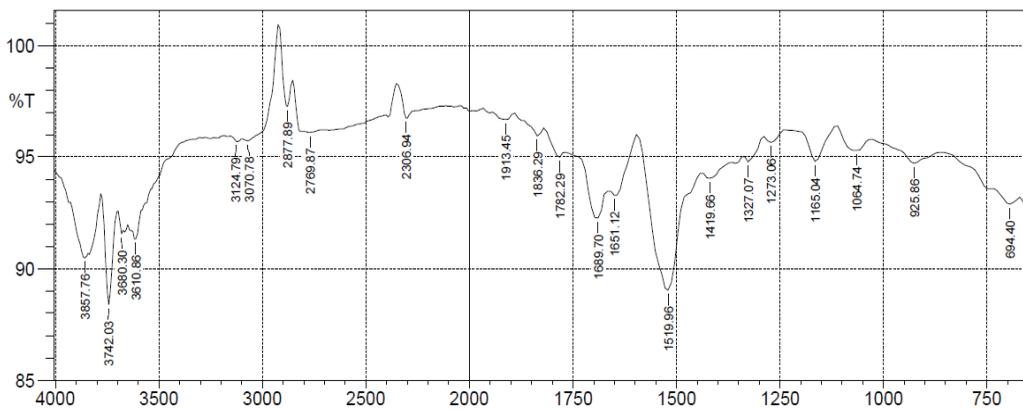Fig. 3a: FTIR of untreated sample.

Fig. 3b: FTIR of prepared adsorbent

Full factorial design of experiment was employed to optimize the removal of the thiazole dye from aqueous solution by the prepared adsorbent. Optimization here implies the application of various parameters, which may potentially affect adsorption process to monitor their effects on the removal efficiency of adsorbents. The optimal condition was considered achieved when a combination of these parameters yielded the highest removal efficiency. Table 3 show the variations of the selected factors affecting the adsorption process and their corresponding removal efficiency (response) in percentage, obtained after each experimental run was performed for the adsorption of TD1 onto the adsorbent. From the results obtained, removal efficiency of TZAC was best (99.50%) at pH 5, adsorbent dose of 0.10 g, initial dye concentration of 5.00 ppm for 20 minutes. The analysis of variance (ANOVA) for the adsorption of TD1 onto the prepared adsorbent is presented in Table 4. The statistical analysis carried out showed that all the listed models were well defined to predict the adsorption efficiency of TD1 by the prepared adsorbent. The model F-value observed was 278.34, an indication that the model was significant, also values of Prob>F less than 0.05 reflects that the model terms were significant. The obtained Adeq Precision (which measures the signal to noise ratio) for the adsorbent was greater than 4, suggesting that the model can be used to navigate the design space effectively. CV value obtained was less than 10; this is an indication that the model is reproducible. The R^2 value obtained for the model was high (close to unity), indicating that there is good agreement between the experimental and predicted values for the removal efficiency as suggested by the model. The mathematical regression model for the 16 runs of the factorial design is given by:

Removal efficiency (%)
$$=+74.66-17.84 * A-8.66 * B+7.28 * C-4.53 * D-3.16 * A * B+1.53 * A * C+3.72 * B * C-2.34 * B * D+3.59 * C * D-2.03 * A * B * C+1.78 * A * B * D+1.03 * B * C * D-2.59 * A * B * C * D$$

TABLE 3
Design matrix and response for adsorption of TD1 onto prepared adsorbent

Run	pH(A)	Dose(B) (g)	Conc(C) (ppm)	Time(D) (mins.)	Rem. Eff. (%)
1	10.00	0.10	5.00	60.00	52.00
2	5.00	0.05	1.00	20.00	99.00
3	10.00	0.05	5.00	60.00	76.50
4	10.00	0.05	5.00	20.00	75.00
5	10.00	0.10	5.00	20.00	59.00
6	5.00	0.05	5.00	20.00	98.00
7	5.00	0.10	1.00	20.00	92.00
8	10.00	0.10	1.00	20.00	41.00
9	5.00	0.10	5.00	20.00	99.50
10	5.00	0.05	1.00	60.00	97.00
11	5.00	0.05	5.00	60.00	98.00
12	5.00	0.10	5.00	60.00	97.50
13	10.00	0.05	1.00	20.00	70.00
14	10.00	0.10	1.00	60.00	28.00
15	5.00	0.10	1.00	60.00	59.00
16	10.00	0.05	1.00	60.00	53.00

TABLE 4
ANOVA for the Factorial model of TD1 removal by prepared adsorbent

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	8424.20	13	648.02	278.34	0.0036	significant
A	5094.39	1	5094.39	2188.19	0.0005	
B	1198.89	1	1198.89	514.96	0.0019	
C	848.27	1	848.27	364.36	0.0027	
D	328.52	1	328.52	141.11	0.0070	
AB	159.39	1	159.39	68.46	0.0143	
AC	37.52	1	37.52	16.11	0.0568	
BC	221.27	1	221.27	95.04	0.0104	
BD	87.89	1	87.89	37.75	0.0255	
CD	206.64	1	206.64	88.76	0.0111	
ABC	66.02	1	66.02	28.36	0.0335	
ABD	50.77	1	50.77	21.81	0.0429	
BCD	17.02	1	17.02	7.31	0.1139	
ABCD	107.64	1	107.64	46.23	0.0210	
Residual	4.66	2	2.33			
Cor Total	8428.86	15				

Std. Dev.	1.53	R-Squared	0.9994	
Mean	74.66	Adj R-Squared	0.9959	
C.V.	2.04	Pred R-Squared	0.9646	
PRESS	298.00	Adeq Precision	50.840	

The factors selected had varying effects on the dye removal efficiency of the prepared adsorbent. Looking at three factors interactive effect, the adsorbent showed optimal TD1 removal of 98.50% (Fig. 4) at low pH, low level adsorbent dose and high level initial dye concentration; 98.41% TD1 removal is obtainable at low level pH, adsorbent dose and contact time respectively (Fig. 5), while low level adsorbent dose, high level initial dye concentration and high level contact time results in 87.25% TD1 dye removal by TZAC (Fig. 6). According to the design, the optimal conditions as well as the experimental and predicted values obtained are summarized in Table 5.
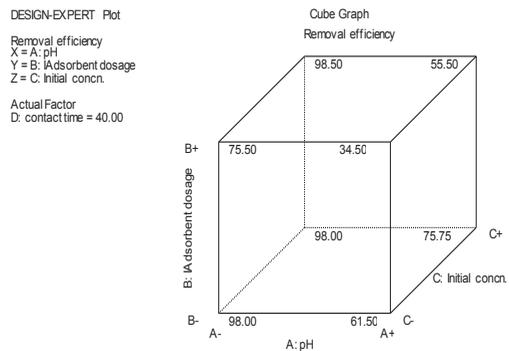

Fig. 4: Three factor-interactive effect for the removal of TDI at low level pH, lowlevel adsorbent dose and high level dye concentration
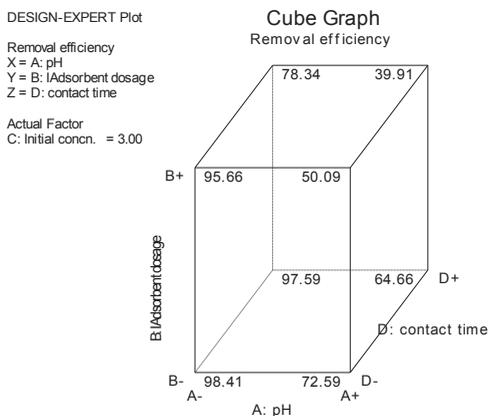
Fig. 5: Three factor-interactive effect for the removal of TDI at low levels of pH, adsorbent dose and contact time
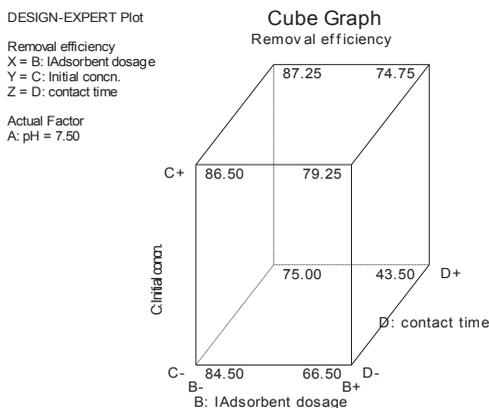

Fig. 6: Three factor-interactive effect for the removal of TDI at low level of adsorbent dose, high level initial dye concentration and high level contact time

TABLE 5
Model validation

pH	Dose (g)	Conc (ppm)	Time (mins.)	Removal efficiency exprmental (%)	Predicted (%)
5.00	0.10	5.00	20.00	99.50	99.94

Conclusion

In the present study, adsorbent prepared from fluted pumpkin seed waste was used for the removal of 5-amino-4-hydroxy-3-[(E)-(5-nitro-2-thienyl)diazenyl]-2,7-naphthalenedisulfonic acid mono sodium from aqueous solution. A 2-level full factorial design of experiment was used to study the effect of pH, adsorbent dosage, initial dye concentration and contact time, on the removal efficiency of the dye by the adsorbent. It was found that the factors selected had varying effect on the dye removal efficiency of the prepared adsorbent. The optimal condition was obtained when the adsorbent dosage was 0.10 g, initial dye concentration 5.00 ppm, pH 5 and time of contact 20 minutes. In such combination of parameters, the removal efficiency was 99.50%, which was higher than values reported for some adsorbents. The present research shows that fluted pumpkin seed waste can serve as precursor for preparing adsorbent of good qualities, capable of removing azo dyes from aqueous solutions.

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