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Batch adsorptive removal of metanil yellow from simulated dye wastewater using nitric acid modified-H_3PO_4-activated carbon (NAMPAAC) from *Gmelina arborea* bark: equilibrium and isotherm studies

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ABSTRACT

The aim of this work was to investigate the capacity of nitric acid modified-H_3PO_4-activated carbon produced from *Gmelina arborea* bark in the removal of metanil yellow from aqueous solution. The effects of initial dye concentration, C_0, contact time, adsorbent dosage, and initial solution pH on the adsorption capacity q_e were studied. Experimental data were analyzed with the Langmuir, Freundlich, Flory–Huggins and Temkin isotherm models. Results show low equilibrium adsorption capacities which decreased with increase in C_o. The optimum experimental q_e obtained was 2.35 mg/g by C_o 25 mg/L. The optimum contact time of 300 min was obtained. Correlation coefficient R^2, values (0.861–0.9781) obtained, show that the four applied isotherm models analyzed experimental data well. The optimum pH and adsorbent dosage were 2 and 0.01 g/25 mL solution, respectively. The ΔG_{ads} value of –11.248 kJ/mol based on the Flory–Huggins isotherm, and the separation factor, R_L values 0.489, 0.332, and 0.199 for C_o 25, 50, and 100 mg/L, respectively, show the adsorption to be spontaneous and favourable. The H_3PO_4-activated carbon was modified with nitric acid, to determine the effect of the modification on the surface area and adsorption capacity. Compared with a similar work with unmodified H_3PO_4-activated carbon (yet unpublished), there was a decrease in surface area, and q_e by 109.59 m^2/g and 12.363 mg/g, respectively. These results show that the modification of the activated carbon with nitric acid had a negative effect.

Keywords: Activated carbon; Adsorption capacity; Batch adsorption; *Gmelina arborea* bark; Isotherm models; Metanil yellow

1. Introduction

Dyes are used extensively in many industries such as textile, pharmaceutical, paper, plastic, and tannery, to colour their products. The textile industry is the largest consumer of dyes among these industries. About 10,000 different textile dyes with an estimated annual production of 7 × 10^5 metric tons are commercially available [1]. Dye-bearing wastewaters exhibit high colour and high chemical and biochemical oxygen demands. The discharge of these dyes effluents in the environment is worrying for both toxicological and esthetical reasons [2]. Azo dyes once released into water bodies, produce toxic amines by the reductive cleavages of azo linkages. These degradation products cause severe harmful effects on human beings through damaging the vital organs such as the brain, liver, kidneys, and reproductive systems. They also prevent photosynthetic activity in aquatic plants by reducing light penetration [3]. Visual pollution is a serious problem in water quality. It is not easy to accept red or brown rivers [4].

Due to the worries created by the pollution of water bodies with dye wastewaters, a number of methods with varying degrees of success have been developed. They include coagulation, foam floatation, filtration, ion exchange, sedimentation, solvent extraction, electrolysis, chemical oxidation,

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chemical precipitation, and membrane process. All these methods have shortcomings and limitations. For example, coagulation requires pH control, and causes further problems of sludge disposal. Ozonation does not minimize chemical oxygen demand [3].

The separation method based on adsorption is a promising method because it is non-denaturing, highly selective, energy efficient, and relatively inexpensive. Adsorption is a surface phenomenon where a substance binds to the surface of another on atomic or molecular scale [5]. Batch experiments are usually carried out to measure the effectiveness of adsorption for removing specific adsorbates, as well as to determine maximum adsorption capacities [6]. Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure, which are available as granules, extruded pellets, fibres, etc. Activated carbons remain the most used adsorbents, mainly due to their superior physical and chemical properties, such as highly developed porous structure, large specific surface area, good mechanical properties, biocompatibility, and chemical stability, as well as their low cost and great accessibility [7].

Wastewater treatment by adsorption using activated carbons is very effective and has been cited by United States Environmental Protection Agency (USEPA) as being one of the best available environmental pollution control technologies. However, the widespread use of activated carbon adsorption is still restricted because of the high costs of commercial carbons. This is due to the use of non-renewable and relatively expensive starting materials such as coal which is expensive, thereby making pollution control costly. Many recent studies have focused on the use of renewable and cheaper precursors, mainly agricultural wastes and by-products [8–10], such as water spinach [11], cassava peels [12], banana stalk [13], plum kernels [14], cocoa pod husk [15], oil palm fibre [16], groundnut hull [17], and hen feathers [18] as raw materials in the production of activated carbons.

Metanil yellow is a synthetic azo dye applied on wool, nylon, silk, paper, ink, aluminium, detergent, wood, fur, cosmetics, and as biological stain. It is hazardous when ingested and slightly hazardous when inhaled or contacts the eyes [19]. Toxicity data reveal that oral feeding or intraperitoneal and intratesticular administration of metanil yellow in animals produces testicular lesions causing seminiferous tubules to suffer damage, and decreased rate of spermatogenesis. Oral consumption of metanil yellow leads to methaemoglobinaemia [20] and cyanosis [21] in humans, while skin contact results into allergic dermatitis [22]. Metanil yellow has tumour-producing effects and can cause intestinal [23] and enzymic [24] disorders in the human body. It is not mutagenic but can alter the expressions of genes [25].

Gmelina arborea grows abundantly in Nigeria. It is mainly used as timber. The bark is not useful industrially, hence, the bark constitutes a huge waste in the environment. The aim of this work was to produce H_3PO_4-activated carbon from *G. arborea* bark, modify it with nitric acid, and use it to remove metanil yellow, an anionic dye, from aqueous solution by batch adsorption. The modification with nitric acid was to study its effect on the surface area and q_e of the adsorbent.

2. Materials and methods

2.1. Preparation of metanil yellow solution

The metanil yellow also called C.I. Acid Yellow 36 (M/s. Merck, Switzerland), used in this study, was bought at Onitsha, Anambra State, Nigeria, and used directly without further treatment. The structure of metanil yellow, an anionic azo dye is shown in Fig. 1. The stock solution was prepared by dissolving 1 g dye per litre solution using distilled water. Different solution concentrations (25–100 mg/L) used in this adsorption study were obtained by dilution. 0.1 M HNO_3 and 0.1 M NaOH solutions were used for pH adjustments.

2.2. Preparation of activated carbon

The dry *G. arborea* bark biomass was obtained from the trees at Owerri, Nigeria. It was washed three times with distilled water and dried under the sun. The biomass was ground and soaked in 20% w/w H_3PO_4 at a ratio 3 parts H_3PO_4:1 part biomass by mass for 24 h. Excess acid was filtered off and the biomass dried. The dry biomass was carbonized at 450°C–500°C for 7 h. After cooling, the carbon was washed with hot distilled water until filtrate pH was about 6. The washed carbon was dried in a hot-air oven at 110°C for 2 h. After cooling, the carbon was soaked in 0.1 M HNO_3 at a ratio 3 HNO_3:1 carbon w/w for 4 h. Excess acid was filtered off and the carbon washed to about pH 6 with hot distilled water. The washed carbon was dried in a hot-air oven at 110°C for 2 h. It was then cooled and sieved to obtain 0.42–0.841 mm carbon particles. The carbon was stored in an air-tight plastic container.

2.3. Characterization of the activated carbon

The bulk and dry densities, and the porosity of the carbon were determined by the method of Ekpete [26]; pore volume by the method of Mohammed et al. [27]; specific surface area by the ethylene glycol monoethyl ether method [28], iodine number by the Gimba and Musa method [29]; pH by the American society for testing and materials (ASTM) D3838-80 standard test method [30]; moisture, volatile matter, ash, and fixed carbon contents by the methods of Rengaraj et al. [31]; Association of official analytical chemists (AOAC) method [32]; and Isiuku [33]. The point of zero charge, pH_{pzc}, was determined by the solid addition method [1]. In this method, 40 mL portions of 0.1 M KNO_3 solution were introduced into eleven 100-mL conical flasks. The pH values of the solution in the flasks were adjusted to 2–12 with 1 M HCl and 1 M NaOH solutions. 0.2 g portions of nitric acid modified-H_3PO_4-activated carbon (NAMPAAC) were added into the flasks which were then put in a water-bath shaker and agitated at 125 rpm for 5 h at 30°C and atmospheric pressure. The pH values of the supernatants were measured. Values of ΔpH were plotted against initial pH values. The point the plot cut the initial pH axis is the pH_{pzc}. $\Delta pH = pH_f - pH_i$, where pH_f and pH_i are the final and initial pH values.

2.4. Batch adsorption study

Batch adsorption investigations [34] were carried out by shaking 25 mL portions of known initial concentrations

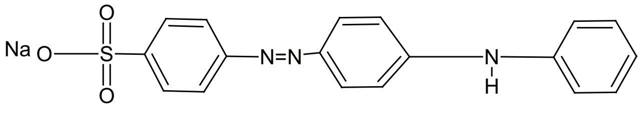

Fig. 1. Structure of metanil yellow.

of metanil yellow solution with 0.01 g portions of carbon in 50 mL flasks. The effect of solution initial pH on the adsorption of the dye solution by NAMPAAC was studied by contacting 25 mL portions of 25 mg/L dye solution with 0.02 g carbon portions in various flasks of varying pH values (2–9) at 30°C. The initial solution pH was adjusted by drop-wise addition of 1 M HNO_3 or 1 M NaOH and the pH measured with a pH meter (Ohaus ST 10, M/s. Ohaus, USA). The flasks were stoppered and placed in a water bath shaker shaking at 175 rpm. Samples were withdrawn at 60 min intervals, filtered and the filtrate analyzed with UV/Vis spectrophotometer (Shimadzu UV-752, M/s. Shimadzu, Japan) at 440 nm λ_{max}.

The quantities of metanil yellow adsorbed per unit mass of adsorbent at time t, q_t (mg/g) and at equilibrium q_e (mg/g) were determined using Eqs. (1) and (2):

$$q_t\left(\text{mg/g}\right)=\frac{\left(C_0-C_t\right)V}{1000x} \tag{1}$$

$$q_e\left(\text{mg/g}\right)=\frac{\left(C_0-C_e\right)V}{1000x} \tag{2}$$

where C_0, C_t, and C_e (mg/L) are the liquid-phase concentrations of the dye at time zero, time t, and at equilibrium, respectively. V (cm^3) is the volume of the solution used and x (g) the mass of dry adsorbent used.

3. Results and discussion

3.1. Characterization of activated carbon

The physicochemical properties of the carbon are shown in Table 1. From Fig. 2, it can be seen that the pH_{pzc} of NAMPAAC was 3.4.

3.2. Effects of initial dye concentration and contact time

25 mL portions of metanil yellow solution of initial concentrations (25–100 mg/L) were contacted with 0.01 g portions of NAMPAAC from *G. arborea* bark at 30°C, initial pH 3 and at shaker speed 175 rpm for 360 min. Fig. 3 shows decrease in adsorption capacity with time, reaching equilibrium at 240 min for 25 and 50 mg/L. C_0 100 mg/L showed virtually no adsorption. This might be due to competition among the dye anions for available binding sites on the adsorbent [35,36]. The equilibrium adsorption capacities were 2.35, 0.1, and 0.48 mg/g for 25, 50, and 100 mg/L initial concentrations, respectively.

Table 1
Physicochemical characteristics of HNO_3-treated-H_3PO_4-activated carbon from *Gmelina arborea* bark

Parameters	Value
pH	5.8
Bulk density (g/cm^3)	0.4
Porosity	0.82
Pore volume (cm^3/g)	0.023
Specific surface area (m^2/g)	350.41
Iodine number (mg/g)	53.49
Moisture content (%)	8.7
Volatile matter content (%)	45.4
Fixed carbon content (%)	36.37
Ash content (%)	9.53
Point of zero charge pH (pH_{pzc})	3.4

3.3. Effect of initial solution pH

The efficiency of adsorption is dependent on the pH of the solution, because variation in pH leads to variation in the degree of ionization and the surface properties of the adsorbent [37,38]. 0.02 g portions of adsorbent were contacted with 25 mL of 25 mg/L initial dye concentration at pH values 2–9. Fig. 4 shows decrease in equilibrium adsorption capacity q_e (mg/g) with increase in pH. The optimum pH was 2. At low pH, the surface of the adsorbent is largely protonated. The H^+ ions provide electrostatic attraction between the adsorbent surface and the anionic dye particles which brings about maximum adsorption. At higher pH, the degree of protonation of the adsorbent surface becomes less, resulting in decrease in diffusion and adsorption as a result of electrostatic repulsion [37,39,40]. At pH 9, lowest adsorption occurred as a result of competition between excess $^{-}$OH ions

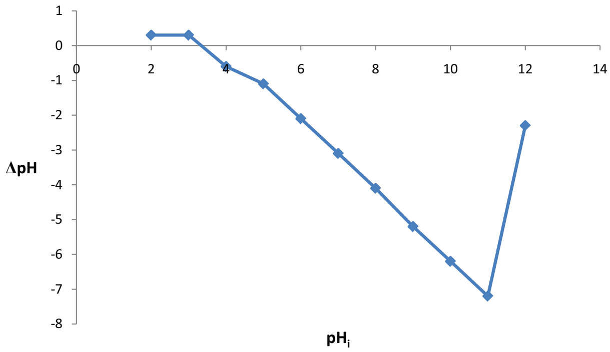

Fig. 2. Point of zero charge pH for NAMPAAC.

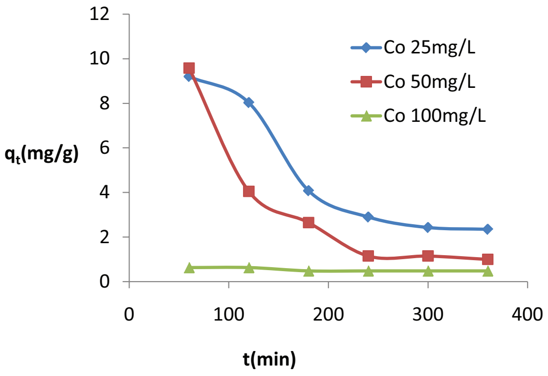

Fig. 3. Adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various initial concentrations.

and the dye anions for adsorption sites [38]. The experimental results show that low pH was favourable for the adsorption of metanil yellow on NAMPAAC from *G. arborea* bark.

3.4. Effect of adsorbent dosage

Different masses of the adsorbent (0.01–0.32 g) were contacted with 25 mL portions of the dye solution at 175 rpm shaker speed, C_0 25 mg/L, pH 3, and temperature 30°C. From Fig. 5, it can be observed that, q_e (mg/g) decreased with increase in adsorbent dosage. The result agrees with the work of Tsai et al. [41] and Pokordi and Vasanth Kumar [42]. The trend can be as a result of splitting effect of flux (concentration gradient) between adsorbate and adsorbent with increasing adsorbent concentration leading to a decrease in the quantity of dye adsorbed per mass of adsorbent [42].

3.5. Adsorption isotherm modelling

An adsorption isotherm shows how adsorbate particles are distributed between the adsorbate and the adsorbent when the adsorption process reaches equilibrium state. Fitting experimental data into various isotherm models is a vital step in looking for the suitable model that can be used for design purposes [43]. Adsorption isotherm is critical in optimizing the use of adsorbents. The Langmuir, Freundlich, Flory–Huggins, and Temkin isotherm models were applied to analyze experimental data in this work. The R^2 values were used to know the fitness of the models.

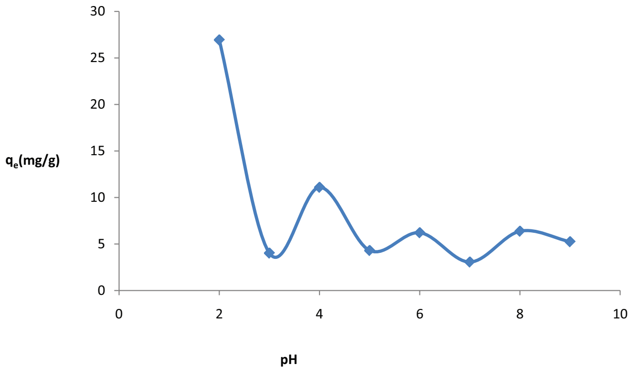

Fig. 4. Adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various pH values.

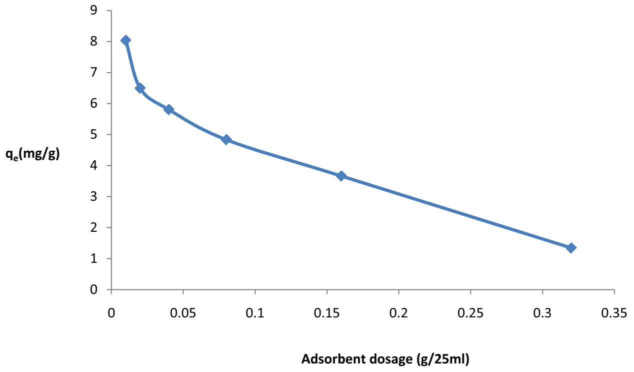

Fig. 5. Adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various adsorbent dosages.

3.6. Langmuir isotherm model

The Langmuir isotherm model assumes the presence of a finite number of binding sites, homogeneously distributed over the adsorbent surface, presenting the same affinity for adsorption of a single layer, and with no interaction between adsorbed species [44]. The well-known Langmuir model equation [45] is expressed as Eq. (3):

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_o (mg/g) is the q_e (mg/g) for a complete monolayer, and K_L (L/g) is a constant related to the affinity of the binding sites and energy of adsorption.

The linear form of Langmuir model equation is expressed as Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_0}{q_o} \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the dye solution, q_e (mg/g) is the amount of the dye adsorbed per unit mass of the adsorbent, q_o (mg/g) is the Langmuir constant related to adsorption capacity and K_L (L/g) is the Langmuir rate constant of adsorption.

A plot of C_e/q_e against C_e gave a straight line with slope $1/q_o$ and $1/q_oK_L$ the intercept (Fig. 6). Table 1 shows the values of q_o and K_L as 0.3724 and 0.0403, respectively, with R^2 0.9781 that shows that Langmuir model analyzed the experimental results well.

The essential characteristics of the Langmuir model can be expressed in terms of a dimensionless constant or separation factor R_L (2) expressed as Eq. (5):

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

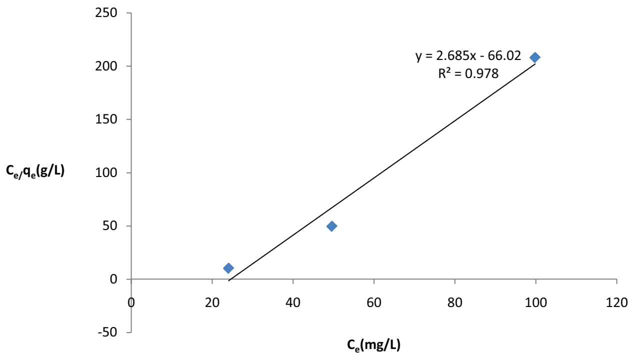

Fig. 6. Langmuir model plot for the adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various initial concentrations.

The value of R_L shows the type of the isotherm to be either favourable ($0 < R_L < 1$); unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 1$). The R_L values for C_0 25, 50, and 100 mg/L were determined to be 0.489, 0.332, and 0.199, respectively, showing the adsorption to be favourable.

3.7. Freundlich isotherm model

The Freundlich equation is empirical and based on adsorption on a heterogenous surface. It is widely used, but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model [46]. The heterogeneous adsorption surface of the adsorbent has unequal available sites with different energies of adsorption [47]. The equation is expressed as Eq. (6):

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F (mg/g) is the Freundlich adsorption or distribution coefficient and $1/n$ a measure of adsorption intensity or surface heterogeneity. $1/n$ ranges between 0 and 1. The closer the value of $1/n$ is to zero the more heterogeneous the surface of the adsorbent is.

The linear logarithmic form of the Freundlich equation is expressed as Eq. (7):

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{7}$$

A plot of $\ln q_e$ against $\ln C_e$ gives a straight line with slope $1/n$ and intercept $\ln K_F$. $1/n$ and K_F were obtained from the slope and intercept, respectively (Fig. 7).

The values of $1/n$, K_F, and R^2 were determined, and are 0.8933, 81.337, and 0.9987, respectively. The values show the Freundlich model a good fit for the analysis of the experimental data.

3.8. Flory–Huggins isotherm model

To explain the behaviour of the surface of the dye anions on the carbon, the fraction of carbon surface covered by dye anions was investigated at pH 3 applying the Flory–Huggins isotherm model. The Flory–Huggins isotherm model [48] is expressed as Eq. (8):

$$\ln\left(\theta/C_e\right) = \ln K_a + n\ln\left(1-\theta\right) \tag{8}$$

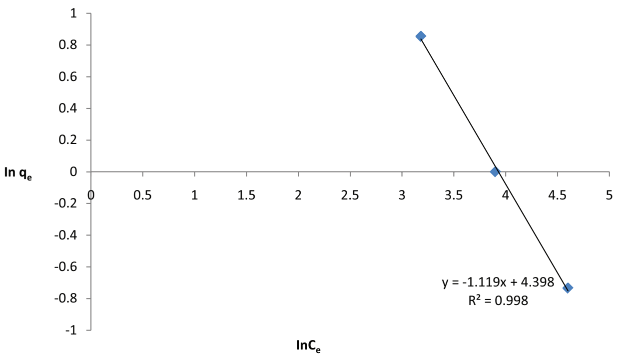

Fig. 7. Freundlich model plot for the adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various initial concentrations.

where θ is the degree of surface coverage, n is the number of dye anions occupying adsorption sites, K_a is equilibrium constant of adsorption, and C_e (mg/L) is equilibrium dye concentration.

A plot of $\ln(\theta/C_e)$ against $\ln(1-\theta)$ gave a straight line with correlation coefficient R^2, n, and K_a values as 0.861, 99.412, and 86.973, respectively (Fig. 8 and Table 2) [49].

Surface coverage (θ) can be calculated from Eq. (9):

$$\theta = \left[1-\left(C_e/C_0\right)\right] \tag{9}$$

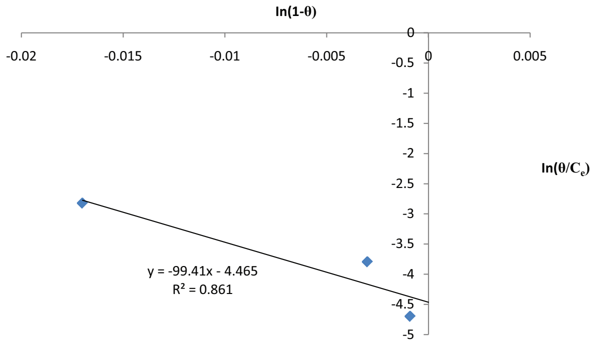

Fig. 8. Flory–Huggins model plot for the adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various initial concentrations.

Table 2
Langmuir, Freundlich, Flory–Huggins and Temkin isotherm models parameters and correlation coefficients

Model	Parameter	Value
Langmuir	q_o (mg/g)	0.372
	K_L (L/mg)	0.0403
	R^2	0.9781
Freundlich	K_F [mg/g (L/mg)$^{1/n}$]	81.337
	n	0.8933
	R^2	0.9987
Flory–Huggins	n	99.412
	K_a	86.973
	R^2	0.861
Temkin	A_T (L/g)	1.582
	b_T (J/mol)	1,191.0471
	R^2	0.943

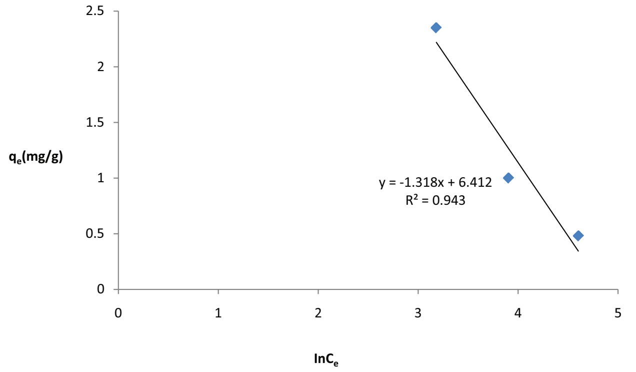

Fig. 9. Temkin model plot for the adsorption of metanil yellow on NAMPAAC from *G. arborea* bark at various initial concentrations.

In order to determine the spontaneity of the adsorption process based on the Flory–Huggins isotherm model, the K_a value was used to determine the change in Gibbs free energy ΔG_{ads}. The ΔG_{ads} value (–11.248 kJ/mol) obtained using Eq. (10) shows a spontaneous adsorption process.

$$\Delta G_{\text{ads}} = -RT\ln K_a \qquad (10)$$

3.9. Temkin isotherm model

The Temkin isotherm [50] considers the effects of indirect adsorbate interactions on adsorption isotherm and assumes that heat of adsorption decreases linearly with coverage due to adsorbate–adsorbate interaction [51]. The model equation is expressed as Eq. (11):

$$q_e = \frac{RT}{b_T}\ln\left(A_T C_e\right) \qquad (11)$$

where b_T (J/mol) is the Temkin isotherm constant related to the heat of adsorption, A_T (L/g) a constant corresponding to the maximum binding energy, R (8.314 J/mol/K) the universal gas constant, and T (K) the Kelvin temperature. A plot of q_e against $\ln C_e$ gives a straight line with slope RT/b_T and intercept $(RT/b_T)\ln A_T$. In this work, b_T and A_T were calculated from the slope and intercept, respectively (Fig. 9). b_T, A_T, and R^2 values were obtained as 1,911.047 J/mol, 1.582 L/g, and 0.943, respectively. The R^2 value shows that the Temkin model fitted experimental data well.

4. Conclusion

Phosphoric-acid-activated carbon from *G. arborea* was modified with nitric acid with a view to study the effect on the q_e of the adsorbent. The optimum q_e was 2.35 mg/g by C_0 25 mg/L, pH 2, and adsorbent dosage 0.01 g/25 mL solution. The optimum contact time was 300 min. The Langmuir, Freundlich, Flory–Huggins, and Temkin isotherm models simulated experimental results well based on R^2 values which were generally above 0.86. The ΔG_{ads} (based on Flory–Huggins isotherm model) and R_L values show that the adsorption was spontaneous and favourable. Compared with a similar work (not yet published) using H_3PO_4-activated carbon from *G. arborea* that was not modified, there were decreases in surface area by 109.59 m^2/g, and q_e by 12.363 mg/g. The modification had a negative effect.

References

[1] L.K. Akinola, A.M. Umar, Adsorption of crystal violet onto adsorbents derived from agricultural wastes: kinetic and equilibrium studies, J. Appl. Sci. Environ. Manage., 17 (2015) 279–288.

[2] T.K. Sen, Removal of cationic dye methylene blue (MB) from aqueous solution by adsorption on biosolid adsorbent, Int. J. Environ. Pollut. Control Manage., 3 (2011) 1–10.

[3] M.A. Oladapo, I.A. Bello, D.O. Adeoye, K.A. Abdulsalam, A.A. Giwa, Sorptive removal of dyes from aqueous solution: a review, Adv. Environ. Biol., 7 (2013) 3311–3327.

[4] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, Dyes Pigm., 69 (2006) 128–136.

[5] R. Sivashankar, V. Sivasurbramanian, A.B. Sathya, S. Pallipad, Biosorption of Hazardous Azo Dye Metanil Yellow Using Immobilized Aquatic Weed, Proc. International Conference on Future Trends in Structural, Civil, Environmental and Mechanical Engineering, Institute of Research Engineers and Doctors, 2013, pp.153–157.

[6] O.B. Isiuku, M. Horsfall Jr., A.I. Spiff, Adsorption of metanil yellow on chemically-activated carbon in a packed-bed column: effect of activation reagent, J. Eng. Appl. Sci., 8 (2013) 282–289.

[7] T. Dobre, O.C. Parvulescu, G. Iavorschi, M. Strescu, A. Stoica, Experimental study of VOCs adsorption onto fixed-bed activated carbon, Analele Universitatii din Oradea Fascicula: Ecotoxicologie Zootechnie si Technologii du Industrie Alimentară, (2010) 1241–1246.

[8] P.D. Rocha, A.S. Franca, L.S. Oliveira, Batch and column studies of phenol adsorption by an activated carbon based on acid treatment of corn cobs, IACSIT Int. J. Eng. Technol., 7 (2015) 459–464.

[9] S. Chakraborty, S. De, S.D. Gupta, J.K. Basu, Adsorption study for the removal of a basic dye: experimental and modeling, Chemosphere, 58 (2005) 1079–1086.

[10] M.J. Martin, A. Artolo, M.D. Balayer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, Chem. Eng. J., 94 (2003) 231–239.

[11] T. Tarawou, D. Wankasi, M. Horsfall, Sorption kinetic study on the removal of Basic Blue–9 dye using activated carbon produced from water spinach, Int. J. Biol. Chem. Sci., 4 (2010) 703–709.

[12] B.O. Isiuku, M. Horsfall Jr., A.I. Spiff, Colour removal from stimulated methyl red wastewater by adsorption on carbon in a fixed bed, Res. J. Appl. Sci., 9 (2014) 201–207.

[13] J.M. Salman, V.O. Njoku, B.H. Hameed, Adsorption of pesticides from aqueous solution onto banana stalk activated carbon, Chem. Eng. J., 174 (2011) 41–48.

[14] R.-L. Tseng, Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation, J. Hazard. Mater., 147 (2007) 1020–1027.

[15] V.O. Njoku, A.A. Ayuk, E.E, Oguzie, E.N. Ejike, Biosorption of Cd(II) from aqueous solution by cocoa pod husk biomass: equilibrium, kinetic and thermodynamic studies, Sep. Sci. Technol., 47 (2012) 753–761.

[16] B.O. Isiuku, O.U. Akakuru, Effect of initial pH on the adsorption of 2,4-dichlorophenol on carbon from oil palm fibre, Niger. J. Appl. Sci., 31 (2013) 170–173.

[17] O.S. Bello, T.A. Fatona, F.S. Falaye, O.M. Osuolale, V.O. Njoku, Adsorption of eosin dye from aqueous solution using groundnut hull-based activated carbon: kinetic, equilibrium and thermodynamic studies, Environ. Eng. Sci., 29 (2012) 186–194.

[18] J. Mittal, A. Mittal, In: S.K. Sharma, Ed., Green Chemistry for Dyes Removal from Water, Scrivener Publishers LLC, USA, 2015, pp. 409–457.

[19] T.N. Nagaraja, T. Desiraju, Effects of chronic consumption of metanil yellow, by developing adult rats, on brain regional levels of noradrenaline, dopamine and serotonin on acetylcholine esterase activity and on operant conditioning, Food Chem. Toxicol., 3 (1993) 41–44.

[20] S.M. Sachdeva, K.V. Mani, S.K. Adval, V.P. Jolpota, K.C. Rasela, D.S. Chadha, Acquired toxic methaemoglobinaemia, J. Assoc. Physicians India, 40 (1992) 239–240.

[21] S.S. Chandro, T. Nagaraja, A food-poisoning outbreak with chemical dye: an investigation report, Med. J. Armed Forces India, 43 (1987) 293–300.

[22] B.M. Hausen, A case of allergic contact dermatitis due to metanil yellow, Contact Dermatitis, 31 (1994) 117–118.

[23] S. Ramachandani, M. Das, A. Joshi, S.K. Khanna, Effect of oral parental administration of metanil yellow on some hepatic and intestinal biochemical parameters, J. Appl. Toxicol., 17 (1997) 85–91.

[24] M. Das, S. Ramachandani, R.K. Upreti, S.K. Khanna, Metanil yellow: a bifunctional inducer of hepatic phase I and phase II xenoblastic-metabolising enzymes, Food Chem. Toxicol., 35 (1997) 835–838.

[25] S. Gupta, M. Sundarrajan, K.V.K. Rao, Tumour promotion by metanil yellow and malachite green during rat hepatocarcinogenesis associated with dysregulated expression of cell cycle regulatory proteins, Tetragon. Carcinog. Mutagen. (2003) 301–312.

[26] O.A. Ekpete, Adsorption and Kinetic Studies of Phenol and 2-Chlorophenol onto Fluted Pumpkin (*Telfairia occidentalis*, Hook) Stem Waste Activated Carbon, PhD Dissertation, University of Port Harcourt, Port Harcourt, Nigeria, 2012.

[27] A. Mohammed, A.A. Aboje, M. Auta, M. Jibril, Comparative analysis and characterization of animal bones as adsorbent, Adv. Appl. Sci. Res., 3 (2012) 3089–3096.

[28] A.B. Cerator, A.J. Luteneger, Determination of surface area of fine grained soils by the ethylene glycol monoethyl ether (EGME) method, Geotech. Test. J., 25 (2002) 1–7.

[29] C. Gimba, I. Musa, Adsorption of Phenol and Toxic Metals from Textile Effluent, Proc. 28th Annual International Conference of Chemical Society of Nigeria, Vol. 32, 2005, pp. 165–170.

[30] American Society of Testing Materials, Annual Book of ASTM Standard, Vol. 15.01, Refractories, Carbon and Graphic Products, Activated Carbon, ASTM, Philadelphia, PA, 1996.

[31] S. Rengaraj, M. Seung-Hyeon, S. Sivabam, Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon, Waste Manage., 22 (2002) 534–548.

[32] A.S. Olawale, O.A. Ajayi, M.S. Olakunle, M.T. Ityokumbul, S.S. Adefila, Preparation of phosphoric acid activated carbons from *Canarium schweinfurthii* Nutshell and its role in methylene blue adsorption, J. Chem. Eng. Mater. Sci., 6 (2015) 9–14.

[33] B.O. Isiuku, Adsorption of Metanil Yellow and Methyl Red from Aqueous Solution Using Cassava Peels Activated Carbon in a Fixed-bed Column, PhD Dissertation, University of Port Harcourt, Port Harcourt, Nigeria, 2015.

[34] A.H. Al-Fatlawi, M.M. Neamah, Batch experiment and adsorption isotherm of phosphate removal by using drinking water treatment sludge and red mud, Int. J. Adv. Res. Sci. Eng. Technol., 2 (2015) 557–571.

[35] A.O. Ekepete, M. Horsfall Jr., A.I. Spiff, Removal of chlorophenol from aqueous solution using fluted pumpkin and commercial activated carbon, Asian J. Nat. Appl. Sci., 14 (2010) 321–326.

[36] A. Mahvi, A. Maleki, A. Eslami, Potential of rice husk and rice husk ash for phenol removal in aqueous systems, Am. J. Appl. Sci., 14 (2004) 321–326.

[37] M.R.H. Mas Haris, K. Sathasivam, The removal of methyl red from aqueous solution using banana pseudo-stem fibres, Am. J. Appl. Sci., 6 (2009) 1690–1700.

[38] V.K Gupta, R. Jain, R. Vashney, V.K. Saini, Removal of Reactofix Navy Blue 2 GFN from aqueous solution using adsorption techniques, J. Colloid Interface Sci., 307 (2007) 326–332.

[39] S.D. Khattri, M.K. Singh, Removal of malachite green from dye wastewater using neem sawdust by adsorption, J. Hazard. Mater., 167 (2009) 1089–1094. doi:10.1016/j.hazmat.2009.01.101.

[40] F.A. Baztias, D.K. Sidiras, Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems, Bioresour. Technol., 98 (2007) 1208–1217.

[41] W.-T. Tsai, K.-J. Hsien, H.-C. Hsu, C.-M. Lin, K.-Y. Lin, C.-H. Chiu, Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution, Bioresour. Technol., 99 (2008) 1623–1629.

[42] K. Pokordi, K. Vasanth Kumar, Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fibre carbon: eosin yellow, malachite green and crystal violet single component systems, J. Hazard. Mater., 143 (2006) 311–327. doi:10.1016/jhazamat.2006.09.029.

[43] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed-bed studies, Desalination, 225 (2008) 13–28. doi:10.1016/J.Desal.2007.07.005.

[44] S.F. Montanher, E.A. Oliveira, M.C. Rollenberg, Removal of metal ions from aqueous solutions by sorption onto rice bran, J. Hazard. Mater., B117 (2005) 207–211.

[45] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, J. Shie, Biosorption of methylene blue from aqueous solution by fallen phoenix tree leaves, J. Hazard. Mater., 141 (2007) 156–162.

[46] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, Waste Manage., 21 (2001) 659–702.

[47] A.L. Ahmad, S. Sumathi, B.H. Hameed, Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies, Water Res., 39 (2005) 2483–2494.

[48] M. Horsfall Jr., A.I. Spiff, Studies on the effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Caladium bicolor* (wild cocoyam) biomass, Electron. J. Biotechnol., 7 (2004) 313–323.

[49] M. Horsfall Jr., A.I. Spiff, Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (wild cocoyam) biomass, Electron. J. Biotechnol., 8 (2005) 162–169.

[50] M.J Temkin, V. Pyzhev, Recent modification to Langmuir isotherms, Acta Physiochim., USSR, 12 (1940) 217–222.

[51] V.O. Njoku, A.A. Ayuk, E.E. Oguzie, E.N. Ejike, Biosorption of Cd(II) from aqueous solution by cocoa pod husk biomass, equilibrium, kinetic and thermodynamic studies, Sep. Sci. Technol., 47 (2012) 753–761.