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Rapid, high-capacity and temperature-robust brilliant green adsorption by nitrogen-doped tondolo-derived activated carbon

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Abstract

Nitrogen-doped activated carbon derived from tondolo peels (N-TAC) was synthesised via single-step K_2CO_3 /urea-assisted activation at 700 °C and evaluated for brilliant green (BG) removal from aqueous solution. Nitrogen doping introduced pyridinic, pyrrolic, graphitic and oxidised functionalities, while textural analysis confirmed a high BET surface area of 3504.5 m² g⁻¹ and micropore volume of 1.38 cm³ g⁻¹. N-TAC achieved up to 99.02% BG removal from 50 mL of 50 mg L⁻¹ solution using only 15 mg adsorbent, confirming high efficiency at low dosage. Kinetic experiments at 25, 50 and 75 mg L⁻¹ showed rapid initial uptake followed by slower equilibrium approach. The pseudo-second-order model gave equilibrium capacities of 108.4, 238.4 and 348.6 mg g⁻¹. However, Elovich fitting and Crank/Boyd mass-transfer analysis indicated BG uptake is better described as coupled adsorption-transport involving heterogeneous surface interactions, external mass transfer and internal pore diffusion, rather than purely chemisorption-controlled kinetics. Equilibrium adsorption was evaluated at 298.15, 318.15 and 328.15 K using Langmuir, Freundlich, Temkin, Sips and two-surface Langmuir models. The two-surface Langmuir model gave the best fit, while Freundlich and Sips supported heterogeneous adsorption. No statistically

significant temperature effect was observed across the range, indicating N-TAC maintains performance under thermally variable conditions—highly relevant for practical wastewater treatment, where influent temperatures fluctuate. The highest experimental adsorption capacity was 1820.4 mg g^{-1} at 298.15 K, demonstrating strong practical potential of N-TAC for dye-contaminated water treatment.

Keywords: Nitrogen Doping, Activated Carbon, Adsorption, Brilliant green dye removal, Waste-Peels

1. Introduction

The increasing demand for synthetic dyes across multiple industries, including textiles, paper printing, plastics, and rubber, has raised serious environmental concerns due to the discharge of these compounds into natural water bodies¹. Among various synthetic dyes, Brilliant Green (BG), a cationic triphenylmethane dye, is of particular concern owing to its widespread industrial use, intense colour, and chemical stability².³ Its high-water solubility facilitates rapid dispersion in aquatic environments, while its resistance to biodegradation makes it highly persistent in water systems³. Conventional treatment methods, such as coagulation/flocculation, membrane filtration, and biological treatment, have been applied for its removal; however, these approaches are often limited by high operational costs, incomplete dye removal, or the generation of secondary pollutants⁴. Therefore, developing efficient, cost-effective, and sustainable alternatives for the removal of BG from wastewater has become an urgent environmental priority.

Adsorption is widely recognized as an effective, simple, and economical method for removing dyes from wastewater⁵. Its popularity stems from its high removal efficiency, ease of operation, and the availability of numerous adsorbent materials⁶. Various adsorbents have been investigated, including natural minerals such as clays and

zeolites, biopolymers like chitosan and algae-based biosorbents, agricultural residues such as rice husk and sugarcane bagasse, and advanced carbon nanomaterials including graphene oxide and carbon nanotubes^{6, 7}. Among these materials, activated carbon (AC) remains the most extensively used due to its exceptional physicochemical properties^{8, 9}. It is an amorphous carbonaceous material characterized by a highly developed porous structure and a large specific surface area. Its pore network consists of micropores, mesopores, and macropores, where micropores and mesopores mainly contribute to adsorption, while macropores facilitate the diffusion of adsorbate molecules into the internal structure¹⁰⁻¹³. The adsorption capacity of activated carbon is further enhanced by the presence of oxygen-containing surface functional groups, such as carboxyl, phenolic, carbonyl, and lactone groups, which promote interactions with dye molecules through electrostatic attraction, hydrogen bonding, and π - π interactions^{13, 14}. Moreover, producing activated carbon from low-cost biomass and agricultural waste reduces production costs, promotes waste valorisation, and supports circular economy principles, making it a sustainable option for wastewater treatment^{10, 13}.

The adsorption performance of activated carbon can be further enhanced through the incorporation of heteroatoms into the near-surface carbon framework^{13, 15}. For instance, Nitrogen-doped activated carbons have attracted considerable attention due to their improved physicochemical properties and wide applicability in advanced materials research¹⁶. The introduction of nitrogen atoms into the carbon lattice alters the local electronic structure of the hexagonal carbon network and contributes additional electrons to the π -system of the sp^2 -hybridized carbon framework¹⁷. This modification enhances several key properties of carbon materials, including surface reactivity, electrical conductivity, and adsorption affinity toward various pollutants⁹. Relatively moderate adsorption capacities were reported by Lin

et al. (2023) for N-doped hydrochar derived from biomass, reaching 57.52 mg g⁻¹ for methylene blue (MB) and 62.19 mg g⁻¹ for Congo red (CR)^{18, 19}. Higher adsorption capacities were observed for nitrogen-doped porous carbons prepared from natural leaves by Chen et al. (2018), achieving 626.1 mg g⁻¹ for MB and 620.7 mg g⁻¹ for rhodamine B (RhB)²⁰. Polymer-derived N-doped activated carbons studied by Al-Odayni et al. (2023) exhibited adsorption capacities of up to 405 mg g⁻¹ for methyl orange (MO)²¹. Even higher adsorption performances have been reported for engineered N-doped activated carbons synthesized from waste precursors, with adsorption capacities of 909.09 mg g⁻¹ for Acid Brown 14 (AB14) and 1929 mg g⁻¹ for Acid Orange 7 (AO7) reported by El-Nemr et al. (2024, 2025)^{22, 23}. Additionally, N/O-doped activated carbon prepared from acorn pulp showed a removal efficiency of 94.21% for methylene blue, significantly higher than that of undoped activated carbon (57.60%), as demonstrated by Karadirek et al. (2025)²⁴. These studies collectively demonstrate that nitrogen functionalization can significantly enhance adsorption performance by improving surface chemistry and pore structure. However, nitrogen doping of activated carbon still faces challenges: conventional methods require additional high-temperature steps, increasing energy demand and process complexity, while self-doping, though simpler, often produces lower and uneven nitrogen distributions²⁵. Therefore, strategies that achieve both high nitrogen content and uniform heteroatom distribution with minimal processing are essential to maximize the adsorption performance of N-doped carbons.

In this study, we investigated the adsorption of BG dye using our previously developed nitrogen-doped tondolo-derived activated carbon (N-TAC). Nitrogen-doped activated carbon has rarely been reported for BG adsorption, and our results demonstrate excellent performance, driven by strong interactions between N-TAC and the dye. The physicochemical properties of N-TAC were thoroughly

characterized, and adsorption kinetics, isotherms, and thermodynamics were evaluated, confirming its versatility and highlighting its potential as a sustainable adsorbent for water remediation.

2. Experiments and Methods

2.1 Tondolo peel-derived AC synthesis method

Nitrogen-doped Tondolo-derived activated carbons (N-TAC) were synthesized following our previously published single thermal step carbonization/activation/doping method^{12, 13}. In brief, crushed tondolo peels were mixed with K_2CO_3 and urea at a mass ratio of 1:1:1, then placed in a tube furnace at 700°C for 2 h under Argon flow. The material was subsequently acid-treated (3 M HCl, 5 h), washed to neutral pH, and dried to yield the N-doped activated carbon.

2.2 Characterization

The textural properties of N-TAC were analyzed using a NOVA-Touch LX² (Quantachrome) surface area and pore size analyzer based on the Brunauer–Emmett–Teller (BET) method within a relative pressure range (P/P_0) of 0.05–0.95. Surface morphology was examined using a Zeiss Ultra Plus 55 field-emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 2.0 kV. Raman spectra were obtained using a WITec Alpha 300 RAS+ Raman spectrometer with a 523 nm excitation laser operating at 4 mW and an acquisition time of 120 s. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Escalab 220i-XL spectrometer equipped with an Al K α X-ray source and an energy resolution of 0.6 eV.

2.3 Adsorption experiments

Adsorption experiments were conducted to evaluate the removal performance of the synthesized TAC and the optimized N-TAC using aqueous solutions of BG dye at

different adsorbent doses. The adsorption efficiency of TAC versus N-TAC was first compared using 50 mgL⁻¹ solutions. For dosage optimization, N-TAC was tested at six masses (5, 10, 15, 20, 25, and 30 mg) to establish the optimal removal performance. Adsorption efficiency (% removal) was calculated using equation 1.

$$\text{BG removal \%} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

For kinetic studies, batches containing 10 mg of N-TAC were dispersed in 50 mL BG solutions with initial concentration of 25, 50, and 75 mgL⁻¹ and agitated at 25 °C. Residual BG concentration were determined from UV–Vis absorbance measurements recorded at predetermined time intervals up to 60 minutes.

The adsorption capacities at time t (q_t) were calculated using the following equations¹³:

$$q_t = \left(\frac{C_0 - C_t}{m} \right) \times V \quad (2)$$

Where:

q_t = adsorption capacity (mg g⁻¹) at time t

C_0 = concentration of BG before adsorption time t (mgL⁻¹)

C_t = concentration of BG at time t during adsorption (mgL⁻¹)

V = volume of dye solution (L)

m = Mass of TAC/N-TAC (g)

The adsorption capacity at equilibrium (q_e) was determined as follows¹³:

$$q_e = \left(\frac{C_0 - C_e}{m} \right) \times V \quad (3)$$

Where:

q_e = adsorption capacity at equilibrium (mg g^{-1})

C_0 = concentration of BG before adsorption time t (mgL^{-1})

C_e = concentration of BG at equilibrium (mgL^{-1})

V = volume of brilliant green solution (L)

m = Mass of N-TAC (g)

2.4 Reproducibility

All experimental measurements were conducted in triplicate ($n \geq 3$). Adsorption experiments yielded dye removal standard deviations below 2%.

3 Results and Discussion

The textural properties and morphology of TAC and N-TAC have been characterized in our earlier work and are presented in Figure 1¹³. As shown in Figure 1(a), both materials display Type IVa isotherms with H4 hysteresis loops, which is typical of micro-mesoporous carbons with slit-like pore geometries. N-TAC demonstrates a noticeably higher nitrogen uptake relative to TAC, a trend that correlates well with its enhanced textural properties, including a larger BET surface area and increased micropore volume, as summarized in Table 1. The improved textural properties of N-TAC are linked to the behaviour of urea-derived species during activation. Specifically, the thermal decomposition of urea produces NH_3 and HNCO gases, which serve as additional in-situ activating agents that etch the carbon matrix and generate micropores beyond those formed through K_2CO_3 activation alone^{26, 27}. At the same time, nitrogen incorporation into the carbon framework through C-N bonding helps stabilise pore walls at elevated temperatures, which explains the notably higher micropore volume of N-TAC (1.38 cc g^{-1}) relative to TAC (0.86 cc g^{-1}). These observations are further supported by the pore size distributions in Figure 1(b), which show higher pore volumes

for N-TAC across the micropore region. SEM images in Figures 1(c) and (d), including higher-magnification insets, show a disordered porous carbon structure with interconnected microporous cavities in both samples, which is consistent with what is typically observed in biomass-derived activated carbons. The reproducibility of these textural and morphological features across synthesis batches supports the suitability of tondolo biomass as a reliable activated carbon precursor.

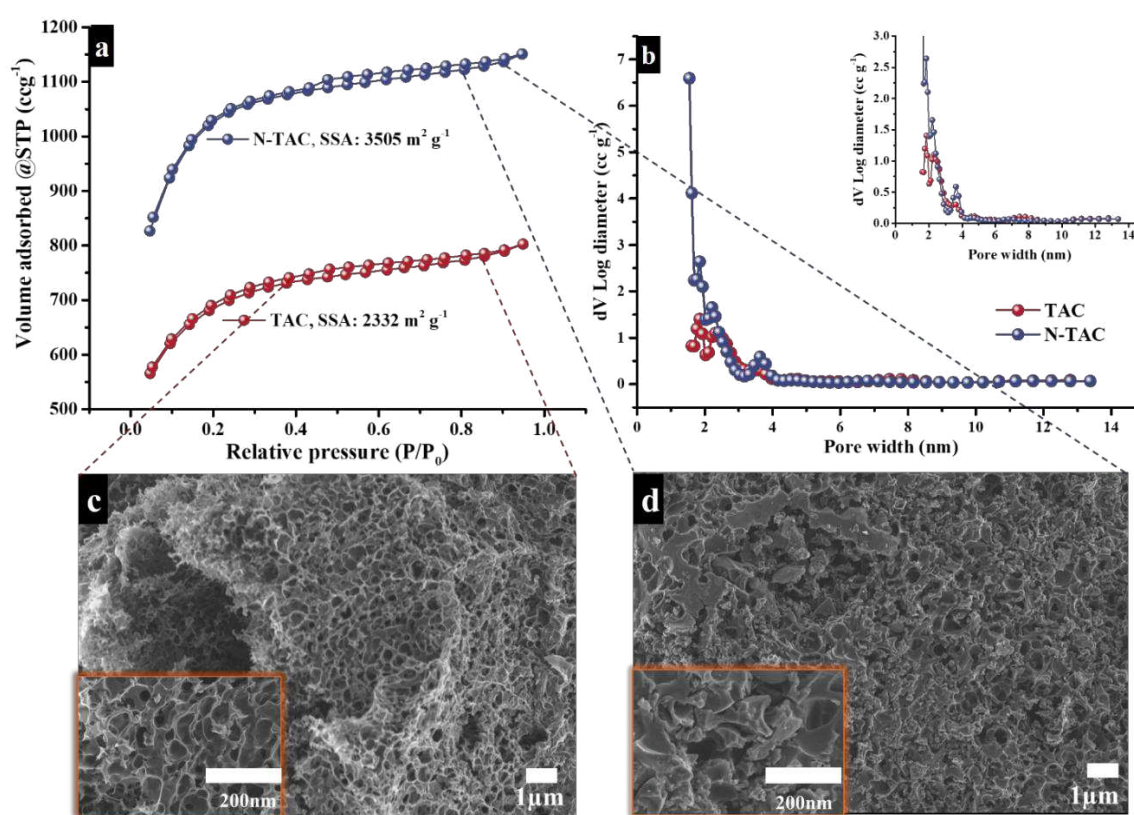


Figure 1 : Textural properties and surface morphology of TAC and N-TAC: (a) N_2 adsorption-desorption isotherms at 77 K exhibiting Type IVa behaviour with H4 hysteresis loops, characteristic of micro-mesoporous carbons with slit-like pore geometries; (b) pore size distribution curves showing enhanced pore volume for N-TAC across the micropore region; (c) and (d) SEM micrographs of TAC and N-TAC, respectively, displaying a disordered, interconnected porous carbon architecture (insets: higher magnification views of the pore structure).

Table 1: Summary of textural parameters for TAC and N-TAC, including micropore volume, total pore volume, and average pore size derived from N₂ adsorption–desorption analysis.

Materials	TAC	N-TAC
Micropore volume (cc g⁻¹)	0.86	1.38
Total pore volume (cc g⁻¹)	1.61	1.61
Average pore size (nm)	2.14	2.04

The structural and chemical composition of N-TAC was investigated using Raman spectroscopy and XPS, with the spectra shown in Figure 2. The Raman spectrum (Figure 2(a)) was deconvoluted into five sub-bands: the D₄ band at 1126.11 cm⁻¹ reflecting sp²–sp³ bonds and amorphous carbon domains, the D₁ band at 1344.84 cm⁻¹ associated with structural disorder from edge sites, vacancies, and heteroatom incorporation, the D₃ band linked to amorphous carbon fragments with the highest peak area (42671.1), and the G₁ and G₂ bands at 1551.86 and 1595.05 cm⁻¹ corresponding to disordered and ordered graphitic sp² carbon domains respectively, confirming a highly defective carbon structure with partially graphitic character typical of biomass-derived activated carbons^{12, 13}. XPS analysis (Figure 2(b)) confirms the presence of carbon, oxygen, and nitrogen on the N-TAC surface, with C 1s deconvolution (Figure 2(c)) revealing graphitic sp² carbon, defective sp² carbon at edge and heteroatom sites, sp³ amorphous carbon, C–O surface groups, and a prominent π–π* satellite feature indicative of aromatic carbon with delocalised electrons, while the O 1s region identifies carbonyl (C=O) and hydroxyl or ether type C–O surface functional groups alongside an Auger satellite contribution^{28, 29}. The N 1s spectrum (Figure 2(d)) reveals four distinct nitrogen configurations, namely pyridinic N (~398.3–398.8 eV), pyrrolic N (~399.6–400.2 eV), graphitic N (~401.0–401.5 eV), and

oxidised N (~402–405 eV), confirming that urea-derived nitrogen was incorporated into the carbon framework in chemically diverse bonding environments, introducing both edge defects and lattice-substituted nitrogen species that are known to enhance surface reactivity and Adsorption performance^{30, 31}.

The combination of these structural and chemical features is expected to enhance N-TAC's adsorption performance significantly³². The high density of defect sites and heteroatom-induced disorder, evidenced by the dominant D-band contributions in the Raman spectrum, creates additional adsorption sites that are not present in pristine graphitic carbons¹⁸. Pyridinic and pyrrolic nitrogen species are known to enhance adsorption capacity for cationic pollutants by introducing localised negative charge density at the carbon surface, thereby promoting electrostatic attraction³³. Graphitic nitrogen enhances electron delocalisation across the carbon framework, strengthening π - π interactions between the adsorbent surface and aromatic pollutant molecules such as dyes and pharmaceutical compounds^{34, 35}. The oxygen-containing functional groups identified in the O 1s region, including carbonyl and hydroxyl groups, further contribute to adsorption through hydrogen bonding and Lewis's acid–base interactions with polar adsorbate molecules³⁶. Collectively, the surface chemistry of N-TAC, characterised by multiple nitrogen-bonding configurations and oxygen-containing functional groups distributed across a highly defective carbon matrix, is expected to yield a material with broad adsorption affinity, enhanced pollutant uptake, and improved performance relative to undoped activated carbons³⁷.

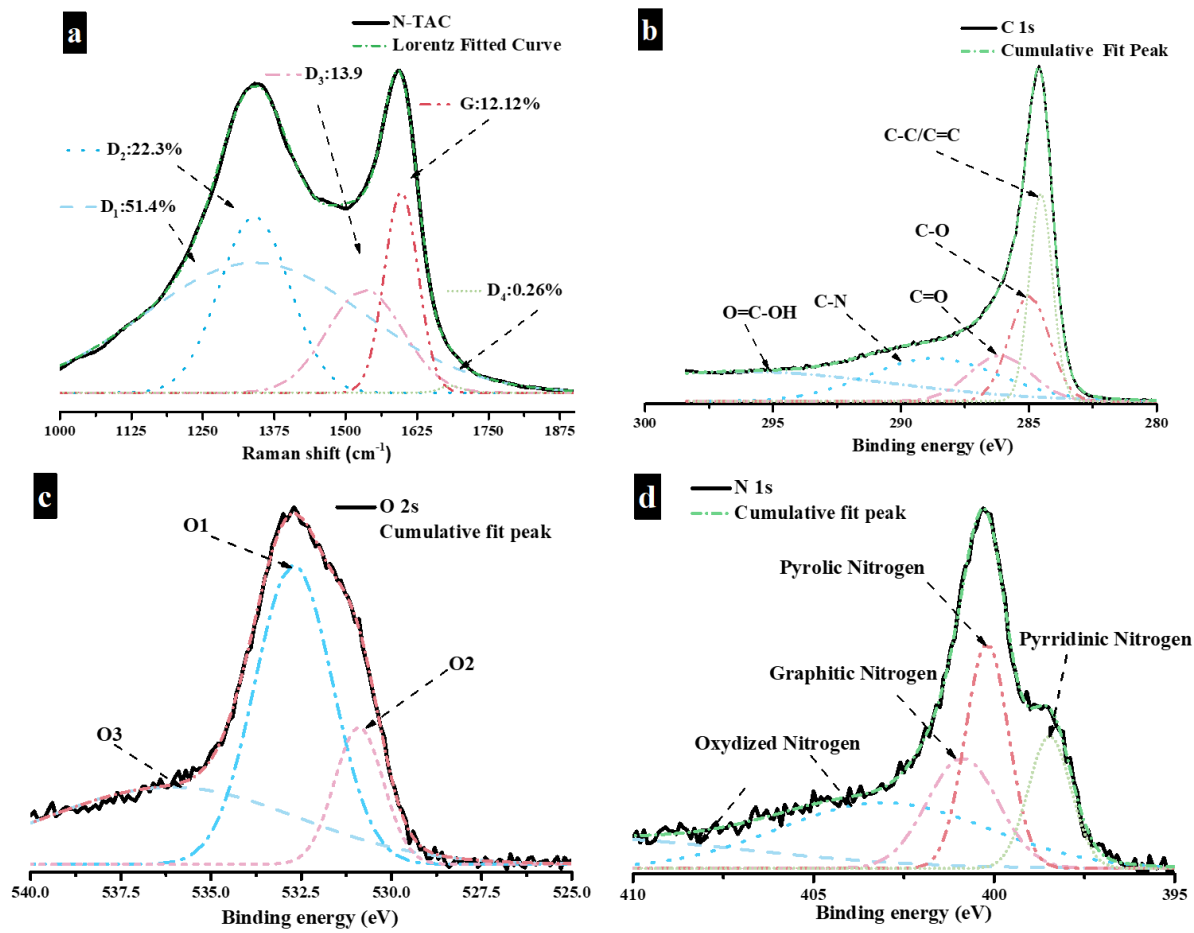


Figure 2: Spectroscopic characterization of N-TAC: (a) Raman spectrum with deconvoluted D and G sub-bands, (b) XPS deconvoluted C 1 spectra showing graphitic defects, (c) deconvoluted O 1s Auger spectra showing oxygen-bonded carbon species, and (d) deconvoluted N 1s spectrum identifying pyridinic, pyrrolic, graphitic, and oxidised nitrogen configurations incorporated into the carbon framework.

Table 2: Raman spectral fitting parameters for N-TAC showing band assignment, peak centre (xc), full width at half maximum (w), peak area (A), reduced chi-squared (χ^2), and goodness of fit (R^2).

Peak	Assignment	xc (cm ⁻¹)	w	A	Reduced χ^2	R^2
Peak 1	D ₁	1126.11	147.57	4596.89	287.85	0.91996
Peak 2	D ₂	1344.84	138.17	10574.44	287.85	0.91996
Peak 3	D ₃	1344.84	224.05	42671.06	287.85	0.91996
Peak 4	G ₁	1551.86	149.15	23640.06	287.85	0.91996
Peak 5	G ₂	1595.05	64.32	9613.06	287.85	0.91996

Table 3: XPS peak fitting parameters for the C KLL, O KLL, and Auger regions of N-TAC, including binding energy, peak width (w), peak area (A), chemical assignment, and goodness of fit (R^2).

Region	Peak	Binding Energy (eV)	Width (w)	Area (A)	Assignment	Chemical significance	R^2
C KLL	1	1202.07	0.91	10937.92	sp ² C Auger	Graphitic carbon domains	0.99968
C KLL	2	1201.61	1.58	9703.68	Defective sp ² C	Edge defects and heteroatom sites	0.99968
C KLL	3	1200.48	2.43	6465.42	sp ³ C	Amorphous carbon contribution	0.99968
C KLL	4	1197.88	5.13	12857.76	C–O component	Oxygen surface groups	0.99968
C KLL	5	1190.32	11.69	20347.36	π – π^* satellite	Aromatic carbon structures	0.99968
O KLL	6	955.7	1.36	1510.89	C=O	Carbonyl surface groups	0.99793
O KLL	7	953.89	2.16	5255.42	C–O	Hydroxyl or ether groups	0.99793
O KLL	8	950.51	6.99	4397.44	O Auger satellite	Oxygen-related energy loss feature	0.99793
Auger	9	1088.21	1.01	317.8	Aromatic C	Conjugated carbon domains	0.99364

Auger	10	1086.31	1.44	1079.63	C–O interaction	Oxygen functional groups	0.99364
Auger	11	1085.21	4.29	932.41	Defective carbon	Structural disorder	0.99364
Auger	12	1079.9	9.19	1133.59	π – π^* shake-up	Delocalized π -electron system	0.99364

Table 4: Binding energy ranges and chemical interpretation of nitrogen species identified from XPS N 1s analysis of N-TAC.

N species	Binding Energy (eV)	Chemical meaning
Pyridinic N	~398.3–398.8	N at graphene edges contributing to defects and active sites
Pyrrolic N	~399.6–400.2	N in five-membered rings associated with structural disorder
Graphitic (quaternary) N	~401.0–401.5	N substituting C in the graphitic lattice improving conductivity
Oxidised N	~402–405	Surface nitrogen oxide groups

The adsorption performance of the tondolo-derived activated carbon (TAC, Figure (a)) was directly compared with its nitrogen-doped analogue (N-TAC, Figure (b)) for the removal of BG dye. Under identical conditions, TAC exhibits good adsorption efficiency; however, N-TAC consistently outperforms the undoped material, demonstrating the beneficial effect of nitrogen incorporation on adsorption behaviour. At a dosage of 5 mg, TAC achieves a removal efficiency of 86.61%, whereas N-TAC already reaches 88.62%, indicating an enhanced affinity at low adsorbent mass loading. This difference becomes more significant at intermediate dosages. For TAC, increasing the mass from 10 to 30 mg results in a plateau at ~98.16%, suggesting early saturation of accessible active sites. In contrast, N-TAC shows a sharper improvement, reaching 98.25% at 10 mg and achieving near-complete removal (99.02%) at 15 mg. Beyond this dosage, the removal efficiency remains constant, indicating that equilibrium has been reached; at this point, nearly all dye

molecules in solution have already been adsorbed, so the number of available adsorption sites exceeds the number of remaining free dye molecules, and further increases in adsorbent mass do not yield additional removal.. This behaviour highlights two key differences between TAC and N-TAC: (i) enhanced adsorption efficiency at lower dosage, and (ii) faster approach to saturation equilibrium for the nitrogen-doped material. The improved performance of N-TAC can be attributed to modifications in surface chemistry induced by nitrogen doping. Specifically, the incorporation of nitrogen functionalities (e.g., pyridinic and pyrrolic groups) increases the basicity and electron density of the carbon surface, thereby strengthening electrostatic interactions with the cationic BG molecules. The observed plateau at higher dosages for both materials is consistent with typical adsorption behaviour, where an excess of adsorbent leads to overlapping or aggregation of active sites and no further increase in removal efficiency ³⁸. Importantly, the plateau is reached at a lower dosage for N-TAC (15 mg) compared to TAC, confirming its superior adsorption capacity.

From an application perspective, the optimal dosage can be identified as 15 mg for N-TAC, which achieves near-complete removal while minimizing material usage. In contrast, TAC requires higher dosages to approach similar performance, making N-TAC a more efficient and economically favourable adsorbent. Overall, these results demonstrate that nitrogen doping not only enhances adsorption capacity but also improves process efficiency, which is critical for scalable water treatment applications.

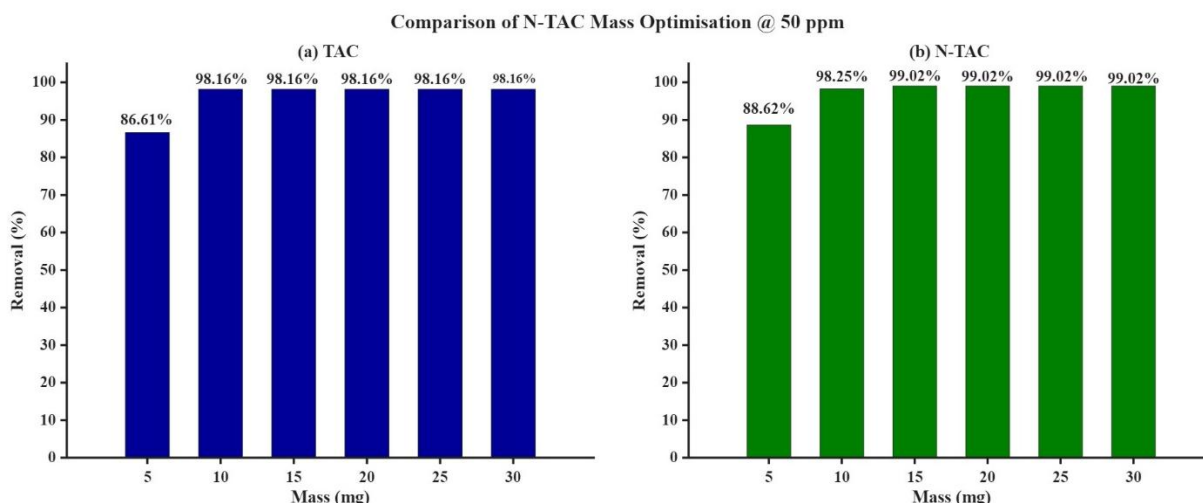


Figure 3: Removal efficiency vs. adsorbent dosage for (a) TAC and (b) N-TAC at 50 mgL⁻¹ BG. N-TAC achieves near-complete removal (~99%) at lower dosage (15 mg) than TAC (~98%), indicating enhanced adsorption due to nitrogen doping.

The adsorption kinetics of BG removal onto N-TAC are presented in Figure 4 and were analysed using pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, Crank internal mass transfer (IMT) and Boyd external mass transfer (EMT) models. The fitting results obtained at initial BG concentrations of 25, 50 and 75 mg L⁻¹ are summarised in Table 5, while the corresponding model fits are shown in Figure 4. The PFO and PSO models were included as widely used empirical adsorption-rate expressions, originally associated with the Lagergren-type first-order formulation and the Ho-McKay pseudo-second-order model, respectively^{39, 40}. The Elovich equation was included because it is commonly used to describe adsorption on heterogeneous surfaces where the adsorption rate decreases progressively as surface coverage increases^{41, 42}. To move beyond purely empirical kinetic descriptions, the Crank and Boyd models were also included to assess internal and external mass-transfer contributions, respectively⁴²⁻⁴⁴.

In all cases, adsorption proceeded rapidly during the initial contact period, followed by a slower approach towards equilibrium. This behaviour indicates that BG uptake initially occurred on readily accessible surface sites, followed by a slower transport-

controlled stage as adsorption progressed within the porous structure of N-TAC. Such multi-stage behaviour is commonly observed for adsorption onto porous carbonaceous materials, where external film transport, rapid surface uptake and subsequent intraparticle diffusion may contribute sequentially or simultaneously to the overall uptake profile ⁴⁵.

The PFO model provided a reasonable description of the kinetic data, particularly at higher initial concentrations, with R^2 values of 0.9281, 0.9882 and 0.9962 at 25, 50 and 75 mg L⁻¹, respectively. The corresponding fitted q_e values were 102.1, 230.6 and 342.8 mg g⁻¹, while k_1 increased from 0.3203 to 0.4272 and 0.5830 min⁻¹. The improvement in the PFO fit at higher concentration reflects the increasingly sharp approach to a plateau in the experimental uptake curves. However, the PFO model remains an empirical rate expression and does not, on its own, distinguish between surface reaction and mass-transfer contributions.

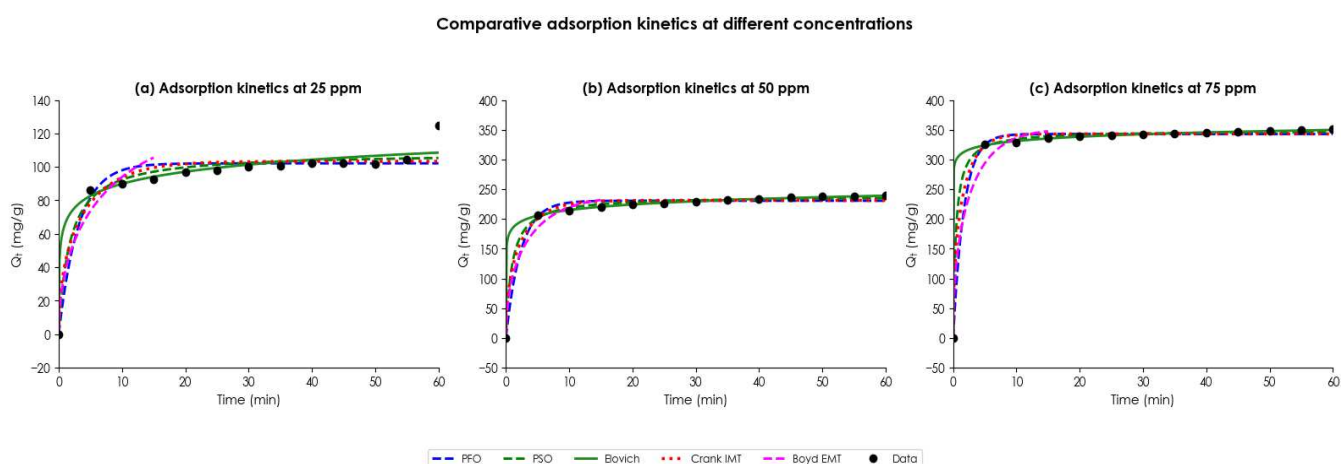


Figure 4 : Adsorption kinetics of N-TAC at initial concentrations of 25 ppm (a), 75 ppm (b), and 100 ppm (c), fitted with pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion, and Elovich models.

Table 5: Kinetic model parameters for BG adsorption onto N-TAC at initial concentrations of 25, 75, and 100 ppm ($T = 298$ K, $pH = 6$, dose = 0.5 g L⁻¹).

Model	Equation	Parameters/Statistics	25 mg L ⁻¹	50 mg L ⁻¹	75 mg L ⁻¹
PFO	$\frac{dq_t}{dt} = k_1(Q_e - Q_t)$	q_e (mg g ⁻¹)	102.1	230.6	342.8
		k_1 (min ⁻¹)	0.3203	0.4272	0.5830
		R ²	0.9281	0.9882	0.9962
		RMSE	7.5316	6.6771	5.6329
		χ^2	7.3075	2.5331	1.2053
PSO	$\frac{dq_t}{dt} = k_2(Q_e - Q_t)^2$	q_e (mg g ⁻¹)	108.4	238.4	348.6
		k_2 (g mg ⁻¹ min ⁻¹)	0.005315	0.004565	0.006643
		R ²	0.9521	0.9968	0.9988
		RMSE	6.1468	3.4596	3.1348
		χ^2	4.7947	0.6997	0.3790
Elovich	$q_t = (1/\beta) \ln(1 + \alpha\beta t)$	α (mg g ⁻¹ min ⁻¹)	5.862×10^3	1.144×10^7	6.817×10^{13}
		β (g mg ⁻¹)	0.09607	0.07423	0.09610
		R ²	0.9667	0.9998	0.9998
		RMSE	5.1270	0.8201	1.1656
		χ^2	3.1992	0.0395	0.0526
Crank IMT	$\frac{\partial Q}{\partial t} = D_e \frac{\partial^2 Q}{\partial r^2}$ With solution 46, 47; $\frac{Q_t}{Q_e} = \sqrt{1 - \exp(Bt)}$ with $B = \frac{\pi^2 D_e}{R_p^2}$	q_e (mg g ⁻¹)	103.3	231.3	343.0
		B (min ⁻¹)	0.1878	0.3055	0.4700
		R ²	0.9358	0.9897	0.9963
		RMSE	7.1191	6.2480	5.5430
		χ^2	7.3733	3.9719	3.7391
Boyd EMT	$\frac{dQ}{dt} = k_B(C_o - C)$ with $k_B = \frac{k_f a}{W}$	k_B (min ⁻¹)	0.0912	0.2015	0.2613
		R ²	0.6492	0.9773	0.9837
		RMSE	16.6353	9.2734	11.6576
		χ^2	31.6422	7.0833	8.2558

Note: PFO = pseudo-first-order; PSO = pseudo-second-order; IMT = internal mass transfer; EMT = external mass transfer. C_o is the initial BG concentration (mg L⁻¹), t is contact time (min), and q_e and q_t are the equilibrium and time-dependent adsorption capacities, respectively (mg g⁻¹). k_1 (min⁻¹) is the PFO rate constant, while k_2 (g mg⁻¹ min⁻¹) is the PSO rate constant. α (mg g⁻¹ min⁻¹) and β (g mg⁻¹) are the Elovich initial adsorption rate and Elovich constant, respectively. For the Crank IMT model, B (min⁻¹) is the lumped intraparticle mass-transfer parameter, related to the effective diffusivity D_e and R_p is the particle radius. Boyd EMT: k_B (min⁻¹) is the external mass-transfer parameter. R², RMSE, χ^2 and AICc were used to evaluate model fit.

The PSO model also described the uptake profiles well, with R² values of 0.9521, 0.9968 and 0.9988 at 25, 50 and 75 mg L⁻¹, respectively. The fitted equilibrium capacities, 108.4, 238.4 and 348.6 mg g⁻¹, were close to the experimentally observed final capacities, supporting the suitability of PSO as an empirical description of the overall adsorption rate. The fitted k_2 values were 0.005315, 0.004565 and 0.006643 g mg⁻¹ min⁻¹ at 25, 50 and 75 mg L⁻¹, respectively. Although PSO is often interpreted as evidence of chemisorption in adsorption studies, this interpretation should be treated cautiously. Azizian (2004) showed that apparent pseudo-order rate constants can arise from combined adsorption and desorption effects and may vary with initial solute

concentration⁴⁸. Therefore, the strong PSO fit in the present study indicates that the equation describes the uptake curve well, but it should not be taken as direct proof that chemisorption is the sole rate-controlling mechanism.

The Elovich model produced the strongest numerical fit at 50 and 75 mg L⁻¹, with R² values of 0.9998 at both concentrations and very low Root Mean Square Error (RMSE) and χ^2 values. At 25 mg L⁻¹, the Elovich model also gave the highest R² among the empirical kinetic models, with R² = 0.9667. This indicates that the Elovich equation captures the rapid initial uptake and subsequent slowing of adsorption particularly well. Since the Elovich model is commonly associated with heterogeneous adsorption-energy distributions, its strong fit supports the presence of non-uniform adsorption environments on the N-TAC surface^{41, 45}. However, the fitted a values increased sharply from 5.862×10^3 to 1.144×10^7 and 6.817×10^{13} mg g⁻¹ min⁻¹ as the initial concentration increased. These extremely large a values suggest that the Elovich parameters are mathematically sensitive to the near-instantaneous early uptake and should not be overinterpreted mechanistically. The fitted β values, 0.09607, 0.07423 and 0.09610 g mg⁻¹, indicate a non-uniform adsorption energy distribution, consistent with heterogeneous adsorption sites on N-TAC.

The Crank IMT model was used to evaluate whether internal mass transfer within the adsorbent particles contributed to the uptake profile. This model is based on the solution to Fick's second law for diffusion-controlled uptake in spherical particles and provides a more transport-aware description than empirical pseudo-order models⁴³. The Crank model provided a good description of the overall uptake behaviour, with R² values of 0.9358, 0.9897 and 0.9963 at 25, 50 and 75 mg L⁻¹, respectively. The fitted lumped internal mass-transfer parameter B increased from 0.1878 to 0.3055 and 0.4700 min⁻¹ with increasing initial BG concentration. This indicates that the overall uptake

profile is strongly influenced by internal transport within the porous adsorbent structure. The good agreement of the Crank model over the full contact-time range supports the interpretation that intraparticle transport contributes substantially to the slower adsorption stage following the rapid initial uptake.

The Boyd EMT model was included as an early-time diagnostic for external film mass transfer. The model gave weaker agreement at 25 mg L⁻¹, with $R^2 = 0.6492$, but fitted the early uptake behaviour better at 50 and 75 mg L⁻¹, with R^2 values of 0.9773 and 0.9837, respectively. The fitted k_b values increased from 0.0912 to 0.2015 and 0.2613 min⁻¹ as the initial BG concentration increased. Since the Boyd model was evaluated primarily over the early-time region, these results suggest that external film transfer contributes mainly during the initial adsorption stage, where the concentration gradient between the bulk solution and the adsorbent surface is largest. However, the Boyd model does not adequately represent the full uptake profile and should therefore be interpreted as a diagnostic of early boundary-layer transport rather than as the primary kinetic model.

Overall, the kinetic analysis indicates that BG adsorption onto N-TAC is rapid and multi-stage. The PSO and Elovich models provide strong empirical descriptions of the uptake curves, while the Crank and Boyd models show that transport effects are also important. The combined evidence suggests an initial rapid uptake of BG onto accessible surface sites, followed by slower internal mass transfer within the pore network. Therefore, the adsorption kinetics should not be attributed solely to chemisorption or to a single rate-limiting process. Instead, BG uptake onto N-TAC is best described as a coupled adsorption and transport process involving heterogeneous surface interactions, early external film transfer and subsequent intraparticle diffusion.

The equilibrium adsorption behaviour of BG onto N-TAC was evaluated using the Langmuir, Freundlich, Temkin, Sips and two-surface Langmuir isotherm models at 298.15, 318.15 and 328.15 K. The corresponding fitting parameters and goodness-of-fit statistics are summarised in Table 6, and the fitted isotherm curves are presented in Figure 5. The isotherm data were analysed using non-linear regression rather than linearised isotherm forms, since linearisation can alter the error structure, bias parameter estimates and distort fitted adsorption constants. Non-linear regression has therefore been recommended for estimating adsorption capacity and affinity parameters from isotherm data, particularly where heterogeneous or multi-site adsorption behaviour may be present⁴⁹.

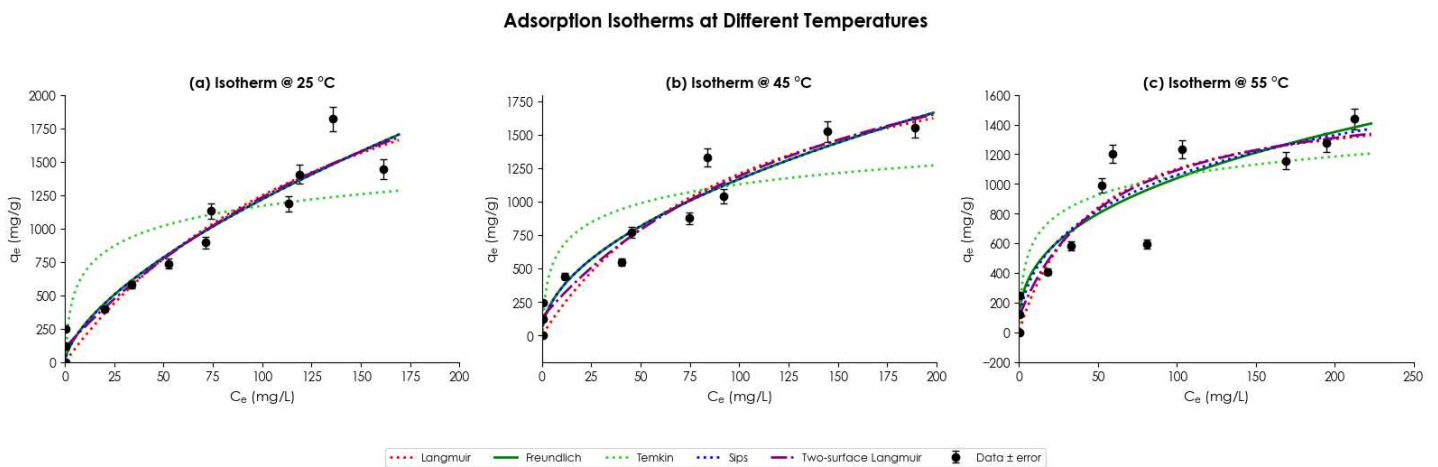


Figure 5: Adsorption isotherms of BG onto N-TAC at 25°C (a), 45°C (b), and 55°C (c), fitted with Langmuir, Freundlich, Temkin, Sips, and Two-surface Langmuir models.

Table 6: Isotherm model parameters for BG adsorption onto N-TAC at 298.15, 318.15 and 328.15 K, with the pooled column representing simultaneous fitting of all valid equilibrium data using one shared parameter set. Experimental conditions: ($C_0 = 20\text{--}200 \text{ mg L}^{-1}$, $\text{pH} = 6$, dose = 0.5 g L^{-1}).

Model	Equation*	Parameter/statistic	298.15 K	318.15 K	328.15 K	Pooled
Langmuir	$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}$	$Q_{\max} (\text{mg g}^{-1})$	3185.5	2496.7	1595.1	2050.6
		$K_L (\text{L mg}^{-1})$	0.00643	0.00938	0.02224	0.01351
		R^2	0.9278	0.9253	0.8545	0.8794
		RMSE	149.0	143.3	183.6	181.2
		χ^2	7062.1	6259.7	4099.3	15798.9
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$K_F (\text{mg. g}^{-1}/(\text{L mg}^{-1})^{1/n})$	65.25	108.58	181.70	136.74
		n	1.573	1.938	2.643	2.181
		R^2	0.9297	0.9398	0.8574	0.8798
		RMSE	147.1	128.7	181.8	180.9
		χ^2	1378.4	653.6	640.2	1964.5
Temkin	$q_e = B \ln(AC_e)$	$A (\text{L mg}^{-1})$	2.267	2.453	2.798	2.504
		$B (\text{mg g}^{-1})$	215.6	205.6	187.2	202.2
		R^2	0.7555	0.8045	0.8000	0.7788
		RMSE	274.3	231.9	215.3	245.4
		χ^2	3508.4	1928.7	1281.6	5648.2

Model	Equation*	Parameter/statistic	298.15 K	318.15 K	328.15 K	Pooled
Sips	$q_e = \frac{Q_{max}(K_s C_e)^m}{1 + (K_s C_e)^m}$	Q_{max} (mg g ⁻¹)	2.11 × 10 ⁶	1.05 × 10 ⁶	3096.0	3891.3
		K_s (L mg ⁻¹) ^{1/m}	8.11 × 10 ⁻⁸	1.93 × 10 ⁻⁸	0.00291	0.00249
		m	0.6360	0.5166	0.5299	0.6260
		R ²	0.9297	0.9397	0.8603	0.8813
		RMSE	147.1	128.8	180.0	179.7
		χ ²	1380.5	654.9	749.8	3209.3
Two-surface Langmuir	$q_e = Q_{max,1} + \frac{Q_{max,2} K_{L,2} C_e}{1 + K_{L,2} C_e}$	$Q_{max,1}$ (mg g ⁻¹)	108.1	132.5	102.0	107.9
		$Q_{max,2}$ (mg g ⁻¹)	3703.2	2718.1	1547.7	2070.9
		$Q_{max,total}$ (mg g ⁻¹)	3811.4	2850.6	1649.6	2178.7
		$K_{L,2}$ (L mg ⁻¹)	0.00437	0.00639	0.01777	0.01049
		R ²	0.9380	0.9445	0.8653	0.8908
		RMSE	138.2	393.9	625.9	1656.8
		χ ²	407.8	132.5	102.0	107.9

***Note:** q_e is the equilibrium adsorption capacity (mg g⁻¹) and C_e is the equilibrium concentration (mg L⁻¹). Q_{max} (mg g⁻¹) is the maximum fitted adsorption capacity. K_L and $K_{L,2}$ (L mg⁻¹) are Langmuir affinity constants. K_F [mg g⁻¹(L mg⁻¹)^{1/n}] is the Freundlich constant, and n is the Freundlich heterogeneity factor. A (L mg⁻¹) is the Temkin equilibrium binding constant for the fitted equation $q_e = B \ln(AC_e)$, while B (mg g⁻¹) is the Temkin constant related to adsorption energy in this empirical form. K_s (L mg⁻¹) is the Sips affinity constant, and m is the Sips heterogeneity parameter. $Q_{max,1}$, $Q_{max,2}$ and $Q_{max,total}$ represent the strongly bound, reversible and total fitted adsorption capacities in the two-surface Langmuir model, respectively. R^2 , RMSE and χ^2 were used to evaluate goodness of fit.

The selected isotherm models were used to test complementary adsorption assumptions. The Langmuir model represents ideal monolayer adsorption on energetically equivalent sites, whereas the Freundlich model provides an empirical description of adsorption on heterogeneous surfaces^{50, 51}. The Temkin model was included as a diagnostic comparison because it accounts for a decrease in adsorption energy with increasing surface coverage⁵². The Sips model combines Langmuir- and Freundlich-type behaviour and is therefore often applied to heterogeneous adsorbents where saturation may occur at higher concentration⁵³. Finally, the two-surface Langmuir model was included to test whether the data were better described by a strongly bound or near-saturated adsorption contribution in combination with a reversible Langmuir-type adsorption contribution⁵⁴. These models are commonly used to distinguish between ideal monolayer adsorption, empirical surface heterogeneity, coverage-dependent adsorption energy, heterogeneous saturation behaviour and multi-site adsorption processes⁵⁵.

The conventional Langmuir model provided a reasonable but not optimal description of the data, with R^2 values of 0.9278, 0.9253 and 0.8545 at 298.15, 318.15 and 328.15 K, respectively. The fitted Q_{max} values decreased from 3185.5 to 2496.7 and 1595.1 $mg\ g^{-1}$ with increasing temperature, while K_L increased from 0.00643 to 0.00938 and 0.02224 $L\ mg^{-1}$. However, these apparent temperature-related trends should not be interpreted on their own as evidence of a thermodynamic temperature effect, because the temperature-specific Langmuir fits were not statistically distinguishable from the pooled Langmuir fit. In addition, the relatively high χ^2 values for the Langmuir model indicate that the model did not describe all concentration regions equally well.

The Freundlich model gave a similar or slightly better empirical description of the data than the Langmuir model, particularly when assessed using χ^2 . The fitted (n) values

were 1.573, 1.938 and 2.643 at 298.15, 318.15 and 328.15 K, respectively. Since ($n > 1$) in all cases, the Freundlich fits indicate favourable adsorption onto a heterogeneous surface. This is consistent with the expected surface complexity of N-TAC, where nitrogen-containing functional groups, pore-size variation and defect sites can create a distribution of adsorption environments for BG molecules⁵⁵.

In contrast, the Temkin model showed the weakest overall agreement with the experimental data. The R^2 values were 0.7555, 0.8045 and 0.8000 at 298.15, 318.15 and 328.15 K, respectively, with higher RMSE values than the other models. This indicates that the simplified Temkin assumption of a linear decrease in adsorption energy with increasing surface coverage does not adequately capture BG adsorption onto N-TAC. The poorer Temkin performance therefore supports the interpretation that the adsorption behaviour is better described by surface heterogeneity and progressive site saturation than by a simple linear coverage-dependent heat-of-adsorption model.

The Sips model did not provide a clearly superior or physically well-constrained fit for all temperatures. At 298.15 and 318.15 K, the fitted $Q_{\max}$ values were extremely large 2.11×10^6 and 1.05×10^6 mg g⁻¹, respectively, while the corresponding K_s values were extremely small. This indicates that the finite saturation capacity was poorly constrained within the experimental concentration range and that the Sips model effectively collapsed towards Freundlich-like behaviour at these temperatures. At 328.15 K, the Sips fit gave a finite $Q_{\max}$ value of 3096.0 mg g⁻¹, but the overall improvement relative to Freundlich was modest. Therefore, although the Sips model remains useful as a heterogeneous adsorption model, its fitted saturation parameters should not be overinterpreted mechanistically in this dataset.

Among the tested temperature-specific models, the two-surface Langmuir model gave the best numerical fit. This model yielded the lowest RMSE and χ^2 values at all three temperatures, with R^2 values of 0.9380, 0.9445 and 0.8653 at 298.15, 318.15 and 328.15 K, respectively. The fitted strongly bound contribution, $Q_{max,1}$, was relatively small, ranging from 102.0 to 132.5 mg g⁻¹, whereas the reversible Langmuir contribution accounted for most of the adsorption capacity. The total fitted capacities were 3811.4, 2850.6 and 1649.6 mg g⁻¹ at 298.15, 318.15 and 328.15 K, respectively. These results are consistent with a heterogeneous adsorption process involving a small high-affinity contribution and a larger reversible adsorption contribution. However, because this model contains an additional parameter relative to the conventional Langmuir model, the improved numerical fit should be interpreted cautiously and supported by statistical comparison rather than by goodness-of-fit statistics alone.

Pooled fits were also obtained by fitting all valid equilibrium adsorption data simultaneously using a single shared parameter set for each model. The pooled two-surface Langmuir model gave the lowest overall RMSE and χ^2 , followed by the Freundlich model. The pooled Sips model gave only a small improvement in RMSE relative to the pooled Langmuir and Freundlich models, while its χ^2 value was higher than that of the pooled Freundlich and two-surface Langmuir models. These results indicate that the combined dataset can be described without assigning separate isotherm parameters to each temperature. The pooled two-surface Langmuir model provides the strongest numerical description, whereas the Freundlich and Sips models support the presence of heterogeneous adsorption behaviour.

Because the fitted isotherms at 298.15, 318.15 and 328.15 K overlapped substantially, additional statistical comparisons were performed to determine whether temperature-specific isotherm parameters were justified. For the conventional

Langmuir model, separate temperature-specific fits were compared with a pooled model in which all temperatures shared common ($Q_{\max}$) and (K_L) values. This nested comparison was performed using an extra sum-of-squares F-test, which evaluates whether the reduction in residual sum of squares obtained by the more complex model is large enough to justify the additional parameters. Allowing independent Langmuir parameters at each temperature did not significantly improve the fit relative to the pooled Langmuir model ($F(4,29)=2.04$, $p=0.115$). Similarly, allowing the two-surface Langmuir parameters to vary independently with temperature did not significantly improve the fit compared with the pooled two-surface model ($F(6,26)=1.51$, $p=0.213$).

Additional empirical isotherm comparisons also did not establish a statistically significant temperature effect. The Freundlich model gave the strongest indication of possible temperature dependence, but the improvement from fitting separate temperature-specific parameters remained just above the conventional 5% threshold ($F(4,29)=2.65$, $p=0.053$). The Sips model did not show a significant temperature effect ($F(6,26)=1.57$, $p=0.197$). Therefore, although some fitted constants changed numerically with temperature, the available data did not provide sufficient statistical evidence that these apparent changes represented a real temperature-dependent adsorption mechanism. The poor practical identifiability of some multi-parameter fits further supports a cautious interpretation, since multi-parameter non-linear models can contain parameters that are not uniquely constrained by the available experimental data; profile-likelihood methods are commonly used to diagnose such practical non-identifiability⁵⁶.

As an additional concentration-normalised comparison, the datasets were analysed by log-log linear regression of q_e against C_e , followed by comparison of the regression

lines using an ANCOVA-type test of slopes and elevations. This approach accounts for the wide range of equilibrium concentrations when comparing the temperature datasets and is appropriate when testing whether regression lines differ in slope or intercept after accounting for a continuous covariate ^{57, 58}. The slopes of the three temperature datasets were not significantly different ($F(2,26)=0.1585$, $p=0.8542$), allowing a common pooled slope of 0.3573 to be used. The elevations or intercepts were also not significantly different ($F(2,28)=0.2231$, $p=0.8015$), giving a pooled intercept of 5.333. Therefore, after accounting for the concentration dependence, the log-log ANCOVA-type comparison provided no evidence that temperature significantly affected either the adsorption trend or the overall magnitude of BG uptake onto N-TAC.

Overall, the combined analysis supports a cautious interpretation. Across the single-surface Langmuir, dual-surface Langmuir, Freundlich and Sips models, no statistically significant temperature dependence could be established. This conclusion was further supported by the log-log ANCOVA-type comparison, which showed no significant differences in either slopes or elevations between the temperature datasets. Therefore, the data show no statistically significant temperature effect within the experimental uncertainty.

Consequently, thermodynamic parameters were not calculated from the apparent temperature-dependent isotherm constants. Such calculations would require clear, systematic and statistically defensible temperature dependence in the fitted equilibrium constants, which was not apparent in the present study. The temperature-specific isotherm models did not significantly improve the pooled fits, the log-log regression comparison showed no significant differences between temperature datasets, and the fitted curve ratios did not support strict practical equivalence. This

interpretation is consistent with the rationale used by Van Veenhuizen et al. (2021)⁵⁹, where the absence of significant differences between adsorption isotherms precluded meaningful calculation of thermodynamic parameters. It is also aligned with critical discussions of adsorption thermodynamics, which note that the standard Gibbs Free Energy (ΔG°), the standard Enthalpy (ΔH°) and the standard Entropy ΔS° calculations require an appropriate dimensionless standard equilibrium constant, as well as a clearly specified adsorption equation and standard state. Direct use of dimensional isotherm constants, such as K_L , K_F or K_S , can therefore lead to ambiguous or misleading thermodynamic quantities⁶⁰.

Notably, the highest experimental adsorption capacity observed in this study was 1820.4 mg. g⁻¹ at 298.15 K, while the corrected model-derived capacities varied depending on the selected isotherm model. This distinction is important because some fitted capacities, particularly the Sips $Q_{\max}$ values at 298.15 and 318.15 K, were not physically well constrained by the experimental concentration range. The high observed adsorption capacity nevertheless remains substantially higher than those values reported for BG adsorption on conventional carbon-based adsorbents, as summarised in Table 7. This highlights the effectiveness of nitrogen doping in enhancing the adsorption performance of tondolo-derived activated carbon, most likely through the introduction of additional active sites and strengthened surface interactions with dye molecules.

Table 7: Comparative performance of biomass-derived and modified carbonaceous adsorbents for Brilliant Green dye removal, highlighting adsorption capacity, kinetic and isotherm models, and thermodynamic behaviour, with emphasis on the superior performance of N-TAC developed in this study.

Adsorbent (Precursor)	Modification	$q_{\max}$ (mg g ⁻¹)	Kinetics (R ²)	Isotherm (R ²)	Reference
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Medlar nucleus AC	Chemical activation	833.15	Pseudo-2nd order	Langmuir	61
Coconut shell AC	NaOH activation	805–1000	Pseudo-2nd order	Langmuir	62
Rosette-like carbon	Ammoniation	357.32	Pseudo-2nd order	Langmuir	63
Noodle waste AC	Microwave + KOH	318.50	Pseudo-2nd order	–	64
Cashew nut shell AC	KOH activation	243.90	Pseudo-2nd order	Langmuir	38
Jamun leaves biochar	Carbonisation	243.90	Pseudo-2nd order	Freundlich	65
Rice straw biochar	Hydrolysed biochar	111.11	Pseudo-2nd order	Langmuir	66
Soybean straw biochar	Pyrolysis	73.50	Pseudo-2nd order	Freundlich	67
Algae biochar	Carbonisation	17.80	Pseudo-2nd order	Langmuir	68
N-TAC (This work)	N-doped activated carbon	1820.4	Pseudo-2nd order	Sips	This study

Thermodynamic parameters were not calculated for BG adsorption onto N-TAC. Although adsorption isotherms were measured at 298.15, 318.15 and 328.15 K, the temperature-specific fitted constants did not provide a statistically defensible basis for van't Hoff analysis. Nested model comparisons showed that allowing the Langmuir, Freundlich, Sips or two-surface Langmuir parameters to vary independently with temperature did not significantly improve the fits relative to pooled models. In addition, the log-log ANCOVA-type comparison showed no significant differences in either slopes or elevations between the temperature datasets. These results indicate that the apparent variation in fitted isotherm constants with temperature was not sufficiently resolved to support calculation of ΔG° , ΔH° or ΔS° .

A further limitation is that several fitted constants were model-dependent and, in some cases, poorly constrained. For example, the Sips model tended towards Freundlich-like behaviour at 298.15 and 318.15 K, producing very large fitted $Q_{\max}$

values and very small K_s values. Similarly, the two-surface Langmuir model gave the best numerical fit but introduced additional parameters that were not statistically justified relative to the simpler models. Therefore, using any of these apparent temperature-dependent constants for thermodynamic analysis would risk overinterpreting fitting artefacts as true thermodynamic trends.

Thermodynamic analysis of adsorption also requires an appropriate dimensionless standard equilibrium constant and a clearly defined standard state. Direct use of dimensional isotherm constants, such as K_L , K_F or K_s , in van't Hoff or Gibbs free energy calculations can produce ambiguous or misleading values⁶⁰. For this reason, and because no statistically significant temperature dependence was established, van't Hoff plots and derived values of ΔG° , ΔH° or ΔS° were not reported. This conservative approach is consistent with previous adsorption studies in which thermodynamic parameters were not calculated when isotherms obtained at different temperatures were not significantly distinguishable⁵⁹, and with critical discussions on the need for dimensionless equilibrium constants in adsorption thermodynamics⁶⁰.

4 Conclusion

This study presents nitrogen-doped tondolo-derived activated carbon (N-TAC), synthesized via a single-step K_2CO_3 /urea activation route, as a fast, high-capacity, and temperature-robust adsorbent for brilliant green (BG) dye removal. The material exhibited an exceptional BET surface area ($3504.5 \text{ m}^2 \text{ g}^{-1}$) and micropore volume ($1.38 \text{ cm}^3 \text{ g}^{-1}$), with XPS confirming pyridinic, pyrrolic, graphitic, and oxidized nitrogen species that enhance interaction with the cationic dye. Dosage optimization achieved 98.25–99.02% BG removal at just 10–15 mg adsorbent per 50 mg L^{-1} dye solution. Kinetic analysis revealed rapid initial uptake followed by slower equilibration, well-described by the pseudo-second-order model (with Elovich giving stronger fits at

higher concentrations). Combined Crank and Boyd modeling indicated that adsorption involves early-stage film diffusion coupled with later-stage intraparticle transport, rather than a single rate-limiting mechanism. Equilibrium data were best fit by a two-surface Langmuir model, reflecting a mix of strong and reversible binding sites, with Freundlich and Sips models corroborating surface heterogeneity. N-TAC achieved a maximum experimental capacity of 1820.4 mg g⁻¹ at 298.15 K—competitive with leading carbon-based adsorbents. Notably, adsorption performance showed no statistically significant temperature dependence across 298.15–328.15 K (confirmed via pooled isotherm fitting and log-log ANCOVA analysis). This thermal stability is a key practical advantage, as it suggests N-TAC can maintain high efficiency in real-world wastewater conditions without temperature control, supporting its scalability for dye-contaminated water treatment.

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