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Removal Kinetics of 2,4,6-Trinitrotoluene from Aqueous Medium by Activated Carbon Obtained from Apple Peel

Elma Kabuğundan Elde Edilen Aktif Karbon ile Sulu Ortamdan 2,4,6-Trinitrotolueni Uzaklaştırma Kinetiği

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ABSTRACT

2,4,6-Trinitrotoluene (TNT) is one of the most commonly used high-powered explosives globally. It causes significant water and soil pollution during production and after use. In this study, the removal kinetics of TNT from aqueous media using activated carbon derived from apple peel (APAC) with a BET surface area of 1429 m^2/g was examined. TNT concentrations were measured using a UV-VIS spectrophotometer by forming a Meisenheimer complex. Pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD) models were employed to analyse the removal kinetics. Among these, the PSO kinetic model more accurately described the adsorption process, with a high correlation coefficient (R^2) and low deviation (%) values. TNT removal efficiency reached 99.7% after 60 min, demonstrating that APAC proved highly effective for TNT removal. The results highlighted its potential as a low-cost and environmentally friendly adsorbent for treating TNT-contaminated wastewater.

Keywords: Explosive, pollution, wastewater, adsorption, Meisenheimer complex

ÖZ

2,4,6-Trinitrotoluen (TNT), dünya çapında en yaygın kullanılan yüksek güçlü patlayıcılardan biridir. Üretimi sırasında ve kullanımından sonra önemli su ve toprak kirliliğine neden olur. Bu çalışmada, 1429 m2/g BET yüzey alanına sahip elma kabuğundan elde edilen aktif karbon (APAC) kullanılarak sulu ortamdan TNT'nin giderim kinetiği incelenmiştir. TNT konsantrasyonları, Meisenheimer kompleksi oluşturarak bir UV-VIS spektrofotometresi kullanılarak ölçülmüştür. Giderim kinetiğini analiz etmek için psödo-birinci mertebeden (PFO), psödo-ikinci mertebeden (PSO) ve parçacık içi difüzyon (IPD) modelleri kullanılmıştır. Bunlar arasında PSO kinetik modeli, yüksek korelasyon katsayısı (R2) ve düşük sapma (%) değerleri ile adsorpsiyon sürecini daha doğru bir şekilde açıklamıştır. TNT giderim verimliliği 60 dakika sonra %99,7'ye ulaştı ve bu da APAC'nin sulu çözeltiden TNT'yi gidermede oldukça etkili olduğunu gösterdi ve sonuçlar, TNT ile kirlenmiş atık suların arıtımı için düşük maliyetli ve çevre dostu bir adsorban olarak potansiyelini vurguladı.

Anahtar Kelimeler: Patlayıcı, kirlilik, atık su, adsorpsiyon, Meisenheimer kompleksi

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INTRODUCTION

2,4,6-Trinitrotoluene (TNT) is a highly effective explosive with a detonation velocity of 6900 m/s and is used as either a primary or a secondary charge in explosives.[1] TNT exhibits several advantageous properties, including good thermal stability (resistance to degradation under heat stress), safe handling, chemical stability (storage for up to 20 years without structural degradation and resistance to moisture), favorable melt-casting

characteristics (melting point 80°C, well below its decomposition or explosion temperature, allowing safe melting and molding), desirable physical properties, and compatibility with other explosives.[2] However, TNT suffers from incomplete oxidation upon detonation owing to a negative oxygen balance (OB (%) = −74%), which adversely affects its performance; therefore, it is often blended with other explosives to improve the oxygen balance (e.g., amatol, composition B, cyclotol, pentolite, tetrytol). Additionally selected physical and chemical properties of TNT are given in Table 1, and its molecular structure and mass spectral ions are shown in Figure 1. Because TNT is relatively insensitive to shock, impact, electrostatic discharge, and friction—factors that reduce the risk of accidental detonation— it is widely used both in military munitions (artillery shells, grenades, aerial bombs, etc.) and in civilian applications (mining, construction, metalworking processes, etc.).[3]

Table 1. Some physical and chemical properties and hazards of TNT.

Chemical formula	$C_7H_5N_3O_6$	Molar mass	227.132 g/mol
Appearance	Pale yellow solid	Density	1.654 g/cm^3
Detonation velocity	6900 m/s	Boiling point	240.0°C
Vapor pressure	0.0002 mmHg (20°C)	Melting point	80.35°C
RE factor	1.00	Signal word	Danger
Pictograms		NFPA 704 (Fire diamond)	

TNT has very low solubility in water (0.13 g/L, 20°C), which makes it suitable for use in humid environments. It has high solubility in organic solvents such as ether, ethanol, and acetone.[4]

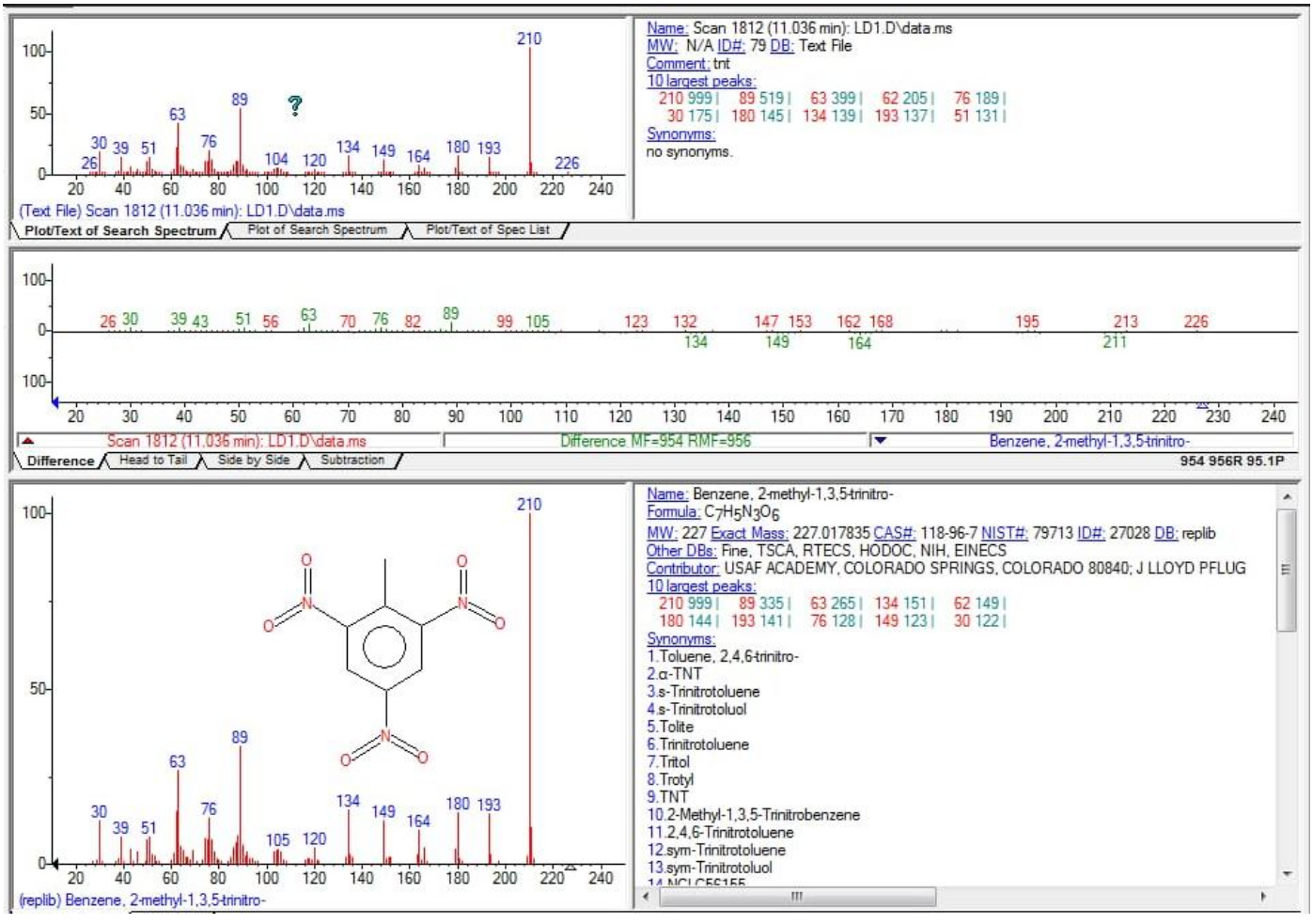

Figure 1. Mass spectrum of TNT.

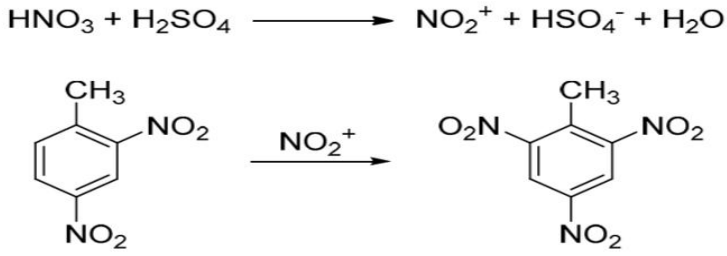

Figure 2. Synthesis stages of TNT[5].

First synthesized by a German chemist in 1861, TNT is produced by the nitration of toluene with nitric acid in three stages, using sulfuric acid as a catalyst. In the first stage, mononitrotoluene (MNT) is obtained; subsequent nitration yields dinitrotoluene (DNT), and finally, trinitrotoluene (TNT) is formed in the effective stage (Figure 2).

Following nitration, crystallization, and sulfation processes are carried out to purify and stabilize TNT. In particular, the wash water generated during sulfation, known as "red water," represents the most significant pollutant discharged into the environment during TNT production.[6] Additionally, wastewater formed during the loading, assembly, and packaging processes of munitions is termed "pink water." Although both "red water" and "pink water" are initially colorless, they undergo photochemical transformations upon exposure to sunlight, turning pink, light red, dark red, or black. "Red water" is extremely toxic and is classified as hazardous waste.[7] TNT is also known to be mutagenic and carcinogenic to humans and animals. Large amounts of TNT red water are produced annually; for instance, in 2022 alone, approximately 5.61 Mt of TNT red water was reported worldwide.[6] TNT exposure has been shown to be mutagenic and carcinogenic to both humans and animals.[8] Even small amounts, as little as 1–2 grams, can be fatal if ingested by humans.[9] Exposure to TNT and DNT can cause serious health problems, including anemia, leukopenia, liver damage, and immune system suppression. Although the maximum permissible TNT concentration in wastewater discharge is less than 0.5 mg/L, this limit is frequently exceeded, posing a severe threat to environmental health (water and soil). Therefore, wastewater containing TNT must be treated using appropriate methods before discharge. Various remediation techniques, including physical[10], chemical[11], and biological[12] approaches, have been applied for TNT removal. Among physical methods, adsorption is particularly attractive because of its ease of application, low cost, and minimal secondary pollution.

In this study, the adsorption technique was applied to remove TNT from aqueous solution using activated carbon prepared from apple peels (APAC), an agricultural waste, as an environmentally friendly adsorbent. The adsorption kinetics of TNT on APAC were investigated by evaluating their fit to different kinetic models. This study expands upon our previous work[13] by applying apple peel-derived activated carbon to the removal of an energetic pollutant (TNT), thereby demonstrating its broader applicability.

METHODS

Preparation of activated carbon

APAC was prepared following the procedure described in our previous study.[13] Briefly, apple peels obtained from the Van region of Turkey were dried and ground, then mixed with $ZnCl_2$ at a weight ratio of 1:1. The mixture was dried and subsequently activated at 500 °C. After washing, filtering, and drying, the product was ground and sieved through a 200-mesh screen.

Preparation of the solution and adsorption studies

A convenient method to quantitatively determine the presence of TNT is UV-VIS spectrophotometry. However, this technique requires the solution to be colored. For colorless samples, a Meisenheimer complex must be formed to generate color[14] (Figure 3).

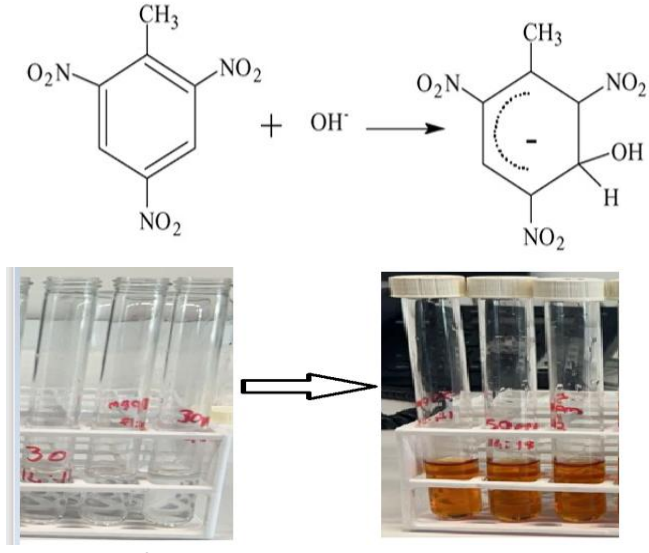

Figure 3. TNT forms Meisenheimer complex in an alkaline medium.

The maximum absorbance wavelength of TNT was determined as 448 nm using a UV-VIS spectrophotometer (Thermo Scientific Evolution 201). To prepare a 100 mg/L (100 ppm) TNT stock solution, a known amount of TNT was first dissolved in a small volume of acetone and then diluted with bi-distilled water. Calibration solutions of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L were prepared by serial dilution of the stock solution with bi-distilled water. Because these solutions were colorless, 1 mL of 1 M KOH was added to 5 mL of each solution to induce Meisenheimer complex formation, thus enabling color development (Figure 3). A calibration curve was then generated based on UV absorbance measurements (Figure 4).

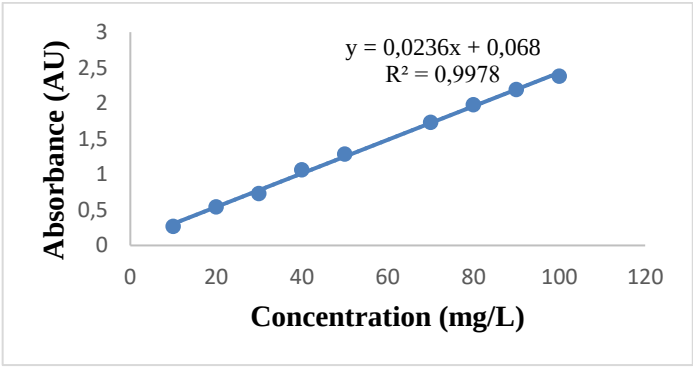

Figure 4. Calibration curve of TNT.

Adsorption experiments were conducted at three initial TNT concentrations (30, 50, and 70 mg/L). In each experiment, 0.2 g APAC was added to 200 mL of the TNT solution. The suspensions were agitated in a temperature-controlled water bath (Thermal H11960) at 25°C and 200 rpm. For kinetic evaluation, samples were withdrawn at specific time intervals (10, 20, 40, 60, 80, 100, and 120 min) and filtered through 0.22 µm syringe filters (GVS, USA). As in the calibration curve procedure, the samples were treated to form the Meisenheimer complex, and UV measurements were performed. All the adsorption experiments were performed in duplicate at the same temperature and stirring speed. The calibration solutions and UV measurements were also carried out in duplicate. The average of the obtained data was used.

The amount of TNT adsorbed by APAC was calculated using the following equation:

$$q_e = [(C_o - C_e) V] / m \quad (1)$$

Where, q_e (mg/g) is the adsorbed amount, C_o (mg/L) is the initial TNT concentration, and C_e (mg/L) is the TNT concentration at equilibrium between the aqueous solution and APAC. m (g) is the mass of APAC, and V (L) is the solution volume.

The percentage of TNT removed from the aqueous solution was determined using the following equation:

$$\text{Removal Efficiency\%} = [(C_o - C_e) / C_o].100 \quad (2)$$

RESULTS AND DISCUSSION

Properties of the APAC

All characterizations of APAC (SEM, FTIR, XRD, BET) were detailed in our previous study.13 Briefly, APAC exhibited a high BET surface area of 1429 m^2/g, an average pore diameter of 2.591 nm, and a cumulative pore volume of 0.653 cm^3/g. FTIR analysis (Figure 5a) confirmed the presence of various functional groups such as C–H group stretching, stretching of the C≡C bond, stretching vibrations of the –C=O and –C=C bonds, C=C stretching rings, symmetric C=O stretching and C-O-C bonds, C–H and C–C stretching rings.[13] XRD patterns indicated both graphite crystallinity and amorphous carbon phases. SEM images revealed a granular and porous surface morphology with pores of varying diameters (Figure 5b).

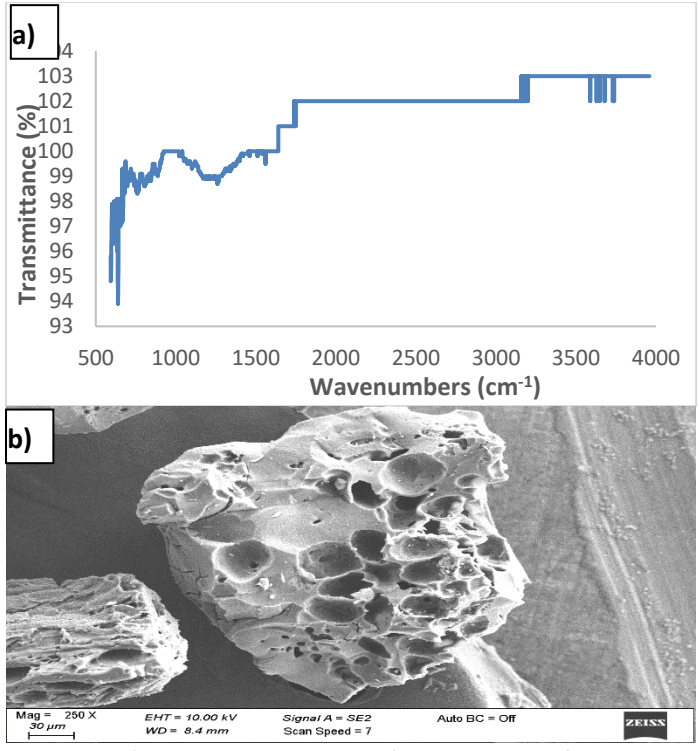

Figure 5. a) FTIR spectrum and b) SEM image of APAC.

Adsorption kinetics

In the adsorption of TNT molecules from aqueous media onto APAC, the process begins with the molecules overcoming film resistance at the liquid–solid interface, followed by film diffusion. Once this step is achieved, intra-particle diffusion can occur. As adsorption proceeds, the active sites become occupied by TNT molecules, and pore saturation gradually slows the process until equilibrium is reached.[15] The variation in TNT concentration in solution and the amount adsorbed on APAC over time is shown in

Figure 6. Rapid adsorption occurred within the first 40 minutes, as the initially vacant pores and active sites were quickly occupied. Adsorption then slowed as saturation approached. The removal efficiency reached 99.7% after 60 minutes but decreased slightly to 98% at 80 minutes, due to minor desorption (release of adsorbed TNT). These high removal efficiencies demonstrate that APAC is highly effective for treating TNT-contaminated water.

For comparison, the literature reports removal efficiencies of 90.6% and 77.2% at 60 minutes for TNT adsorption using nickel oxide (NiO) and copper oxide (CuO) nanoparticles, respectively.[16] Similarly, an indole-based porous organic polymer (PTIM) achieved removal efficiencies above 95% when applied at a dosage of 3 g/L.[17] As shown in Figure 6, TNT concentration in the solution decreased steadily over time, while the amount adsorbed on APAC increased. After 60 min, the q_t value reached 49.83 mg/g at an initial concentration of 50 mg/L.

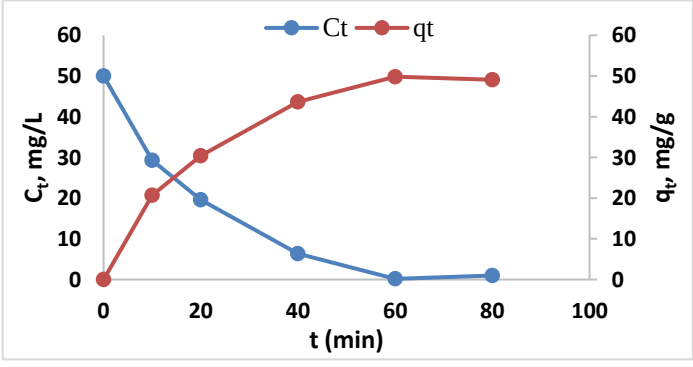

Figure 6. Change in TNT concentration remaining in solution and adsorbed onto APAC over time (initial concentration: 50 mg/L).

The kinetic behavior of adsorption is critical for understanding the underlying mechanisms of the process. To evaluate TNT removal as a function of time, experimental data were fitted to pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD) models.[18] The PFO model assumes that physical adsorption and the occupancy rate of adsorption sites on the surface are directly proportional to the number of unused sites (Equation 3). The PSO model assumes that chemisorption dominates the adsorption process due to electron exchange between the adsorbate and adsorbent (Equation 4). The IPD model describes the transfer of adsorbate to adsorbent particles during the adsorption process via film diffusion, intraparticle diffusion, and adsorption (Equation 5). The corresponding model equations are given below:

$$\ln(q_e-q_t) = \ln q_e - k_1 t \quad (3)$$

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

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

Here; k_1(min^{-1}), k_2($g.mg^{-1}min^{-1}$), and k_i ($gmg^{-1}min^{-1/2}$): are the kinetic rate constants of the PFO, PSO, and IPD models, respectively. t (min) is the contact time, q_t (mg/g), and q_e (mg/g) is the amount of TNT adsorbed on the APAC at any time t and equilibrium, and C is the IPD model constant. Kinetic model parameters and correlation coefficients (R^2) obtained from the slope and intercept values of the plots in Figure 7 are summarized in Table 2.

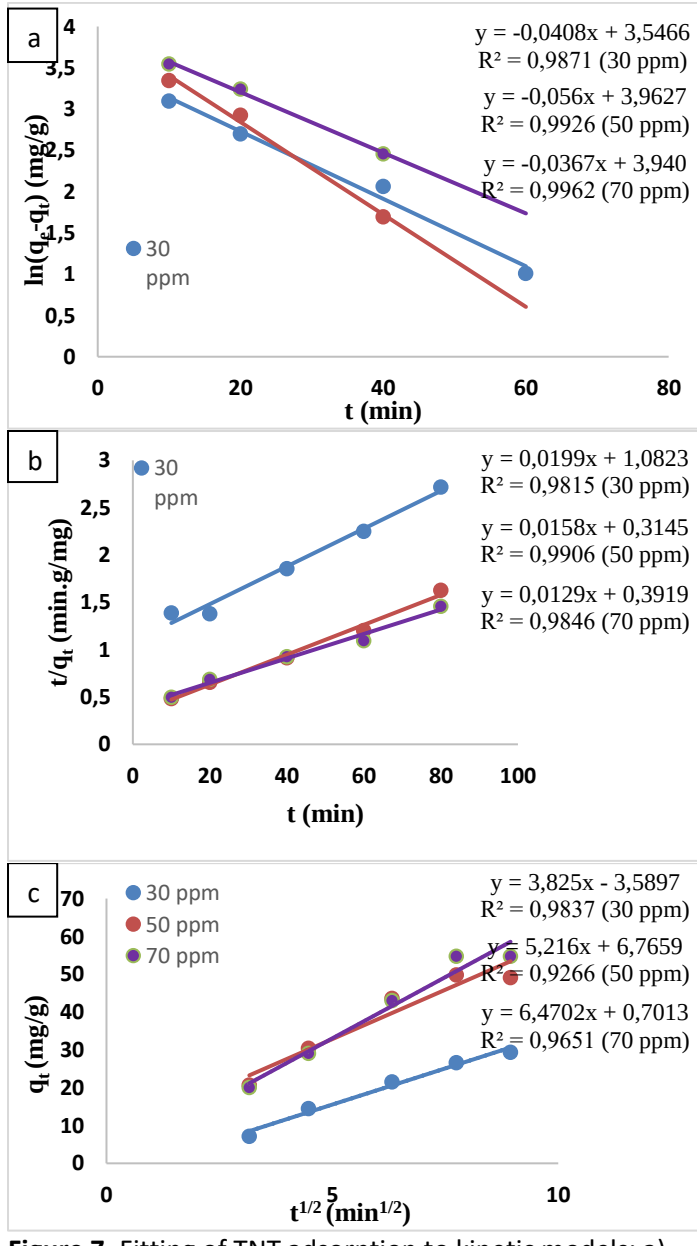

Figure 7. Fitting of TNT adsorption to kinetic models: a) PFO, b) PSO, and c) IPD

Although all three models yielded acceptable R^2 values, those from the PFO model were slightly higher than those from the PSO and IPD models across all initial TNT

concentrations tested. However, when comparing the percentage deviations between the experimental q_e and the calculated q_e from the model, it was evident that the PSO model showed much smaller deviations (Table 2). These results are consistent with previous studies: TNT adsorption onto lignite-based activated carbon was reported to follow pseudo-second-order kinetics.[19], and a similar conclusion was reached for TNT adsorption onto bamboo charcoal, where both external and intra-particle diffusion contributed to the overall process.[20]

In the IPD model, the constant C is associated with boundary layer thickness. A high, non-zero C value indicates that film diffusion also plays a role in the adsorption process, in addition to intra-particle diffusion. An increase in C suggests greater resistance to adsorption. As shown in Table 2, when the initial TNT concentration increased from 30 mg/L to 70 mg/L, the C value decreased from 3.5897 mg/g to 0.7013 mg/g. This reduction in boundary layer thickness indicates that the driving force for mass transfer becomes stronger at higher concentrations, thereby accelerating intra-particle diffusion. Hence, it can be concluded that intra-particle diffusion contributes to the adsorption process but is not the sole rate-controlling mechanism.

Table 2. Kinetic model parameters for the adsorption of TNT on the APAC.

Model	Parameter	30 ppm (mg/L)	50 ppm (mg/L)	70 ppm (mg/L)
	$q_{e,exp}$ (mg/g)	26.6526	49.8306	54.7458
PFO	k_1 (1/min)	0.0408	0.0560	0.0367
	q_e (mg/g)	34.6952	52.5992	51.4186
	R^2	0.9871	0.9926	0.9962
	$q_{e,cal}$ (mg/g)	31.6953	50.7722	45.7327
	%Deviation	18.9201	1.8896	16.4636
PSO	k_2 (g/mg.min)	0.000366	0.000794	0.000425
	q_e (mg/g)	50.2513	63.2911	77.5194
	R^2	0.9815	0.9906	0.9846
	$q_{e,cal}$ (mg/g)	26.3586	47.5248	51.4624
	%Deviation	1.10308	4.6273	5.9975
IPD	k_i (mg/g.min$^{1/2}$)	3.8250	5.2160	6.4702
	C (mg/g)	3.5897	6.7659	0.7013
	R^2	0.9837	0.9266	0.9651
	$q_{e,cal}$ (mg/g)	33.2177	47.1685	50.8188
	%Deviation	24.6321	5.3423	7.1732

CONCLUSIONS

A very high TNT removal efficiency (99.7%) was achieved with APAC. Three different kinetic models were used to evaluate the kinetics of the adsorption process. In conclusion, kinetic analyses revealed that the adsorption data fit the PSO model more accurately than the PFO and IPD models, indicating that chemisorption is the dominant mechanism. The contribution of both film and intra-particle diffusion was also evident. Overall, the results highlight that APAC can serve as a low-cost, environmentally friendly, and highly efficient adsorbent for the remediation of TNT-polluted wastewater.

Etik Komite Onayı: Bu çalışma için etik kurul onayı gerekmemektedir.
Hasta Onamı: Bu çalışma için hasta onamı gerekmemektedir.
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Yazar Katkıları: Fikir, Tasarım, Denetleme, Kaynaklar, Veri Toplanması ve/veya İşlemesi, Analiz ve/ veya Yorum, Literatür Taraması, Yazıyı Yazan, Eleştirel İnceleme: Hülya Koyuncu
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REFERENCES

1. Cohen R, Zeiri Y, Wurzberg E, Kosloff R. Mechanism of thermal unimolecular decomposition of TNT (2,4,6-trinitrotoluene): A DFT study. *J Phys Chem A*. 2007;111(43):11074-11083.
2. Li JS, Chen JJ, Hwang CC, Lu KT, Yeh TF. Study on Thermal Characteristics of TNT Based Melt-Cast Explosives. *Propellants, Explos Pyrotech*. 2019;44(10):1270-1281.
3. Koyuncu H. Patlayıcılar ile ateşli silahların kullanımından kaynaklanan kurşun ve bakır kirliliğinin giderilmesi. *Güvenlik Bilim Derg*. 2024;13(2):437-454.
4. Tisdale JT, Freye CE, Cleveland AH, Scott BL, Hill LG, Duque AL. Investigation of Physical and Chemical Properties of TNT after Spray Drying. *Cryst Growth Des*. 2023;23(9):6902-6908.
5. Kyprianou D, Berglund M, Emma G, et al. Synthesis of 2,4,6-trinitrotoluene (TNT) using flow chemistry. *Molecules*. 2020;25(16).
6. Liu N, Qin J, Ge X, et al. Preparation and study of straw porous biochar with aromatic ring structure for adsorption performance and mechanism toward TNT red water. *Environ Sci Pollut Res Int*. 2023;30(56):118483-118494.
7. Bhanot P, Celin SM, Sreekrishnan TR, Kalsi A, Sahai SK, Sharma P. Application of integrated treatment strategies for explosive industry wastewater—A critical review. *J Water Process Eng*. 2020;35:101232.
8. Mariussen E, Stornes SM, Bøifot KO, Rosseland BO, Salbu B, Heier LS. Uptake and effects of 2, 4, 6 - trinitrotoluene (TNT) in juvenile Atlantic salmon (Salmo salar). *Aquat Toxicol*. 2018;194:176-184.
9. Deng H, Zhang B, Xu Y, et al. A simple approach to prepare isoxazoline-based porous polymer for the highly effective adsorption of 2,4,6-trinitrotoluene (TNT): Catalyst-free click polymerization between an in situ generated nitrile oxide with polybutadiene. *Chem Eng J*. 2020;393:124674.
10. Zhang M, Liu G hua, Song K, et al. Biological treatment of 2,4,6-trinitrotoluene (TNT) red water by immobilized anaerobic-aerobic microbial filters. *Chem Eng J*. 2015;259:876-884.
11. Cotchim S, Thavarungkul P, Kanatharana P, Limbut W. A new strategy for 2,4,6-Trinitrotoluene adsorption and electrochemical reduction on poly(melamine)/graphene oxide modified electrode. *Electrochim Acta*. 2015;184:102-110.
12. Thijs S, Sillen W, Truyens S, et al. The sycamore maple bacterial culture collection from a TNT polluted site shows novel plant-growth promoting and explosives degrading bacteria. *Front Plant Sci*. 2018;9:1-16.
13. Kul AR, Koyuncu H, Turan A, Aldemir A. Comparative Research of Isotherm, Kinetic, and Thermodynamic Studies for Neutral Red Adsorption by Activated Carbon Prepared from Apple Peel. *Water Air Soil Pollut*. 2023;234(6):1-26.
14. Üzer A, Erçağ E, Apak R. Selective colorimetric determination of TNT partitioned between an alkaline solution and a strongly basic Dowex 1-X8 anion exchanger. *Forensic Sci Int*. 2008;174(2-3):239-243.
15. Mdlovu NV, Lin KS, Hsien MJ, Chang CJ, Kunene SC. Synthesis, characterization, and application of zero-valent iron nanoparticles for TNT, RDX, and HMX explosives decontamination in wastewater. *J Taiwan Inst Chem Eng*. 2020;114:186-198.
16. Nanoparticles C oxide, Altalhi AA, Morsy SM, Shaban SA, Ahmed SM. Adsorption of T . N . T . from Wastewater Using Ni-Oxide and. 2021;11(1):43-53.
17. Xu Y, Zhu H, Mo S, et al. Adsorption of 2,4,6-trinitrotoluene by indole-based porous organic polymer with suitable three-dimensional space size via physisorption and chemisorption. *Polymer (Guildf)*. 2024;300:126993.
18. Kokuloku LT, Miensah ED, Gu A, et al. Efficient and comparative adsorption of trinitrotoluene on MOF MIL-100(Fe)-derived porous carbon/Fe composite adsorbents with rod-like morphology: Behavior, mechanism, and new perspectives. *Colloids Surfaces A Physicochem Eng Asp*. 2023;663:131064.
19. Zhang M, Zhao Q, Ye Z. Organic pollutants removal from 2,4,6-trinitrotoluene (TNT) red water using low cost activated coke. *J Environ Sci*. 2011;23(12):1962-1969.
20. Fu D, Zhang Y, Lv F, Chu PK, Shang J. Removal of organic materials from TNT red water by Bamboo Charcoal adsorption. *Chem Eng J*. 2012;193-194:39-49.