

KINETIC AND EQUILIBRIUM STUDY OF TRINITROPHENOL ADSORPTION ONTO POLYANILINE TEA WASTE NANOCOMPOSITE FROM AQUEOUS MEDIUM

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ABSTRACT

The current study is focused on the synthesis of polyaniline-tea waste nanocomposite (PANI-TWC) material as a competent adsorbent for the effective removal of trinitrophenol (TNP) from aqueous medium. Batch experiments were performed to examine the influence of the various adsorption parameters such as pH, dose of adsorbents, contact time and initial concentration of TNP on the adsorption process. The kinetic data were fitted with pseudo-first and pseudo-second-order models, and the kinetic studies were well explained by the pseudo-second-order kinetic model. Moreover, the adsorption isotherm study for TNP adsorption from aqueous solutions on the PANI-TWC was performed by Langmuir and Freundlich isotherm models. The adsorption equilibrium data were best fitted to the Langmuir isotherm, which indicated that the adsorption surfaces are homogeneous and the adsorption occurred in monolayers.

Keywords: trinitrophenol, polyaniline, isotherms, kinetics, nanocomposite

INTRODUCTION

Rapid rate of industrial and urbanization activities has led to an increased disposal of various organic and inorganic pollutants including phenolic compounds into the water which contribute to significant bodies. contamination of the aquatic ecosystem. Nowadays, existence of phenolic compounds in aqueous environment is a growing concern due to their relatively high toxic nature. Among the phenolic compounds, nitrophenols have drawn much attention as they are catalogued as priority toxic pollutants by the United States Environmental Protection

Agency (USEPA) [1]. Aromatic nitro compounds are toxic and exhibit carcinogenic and mutagenic activities since they transform into nitroso intermediates, which are active electrophilic radical nitro-anion, and their Nhydroxy derivative in environment, which have been found equally toxic as nitro aromatics [2]. These products interact with serum albumins, haemoglobins, tissue proteins and DNA, and form adducts [3]. Among the nitrophenols, trinitrophenol (TNP) is highly hazardous and acts as a xenobiotic and is resistant to degradation in environment [4]. It is acidic due to the presence of three electronwithdrawing nitro groups, which stabilize the

phenoxide ion. Moreover, TNP has diverse applications in the syntheses of dyes, explosives, analytical reagents, germicides, fungicides, staining agents, tissue fixatives, tanning agents, photochemicals, pharmaceuticals, and for the oxidation and etching of iron, steel and copper surfaces [1]. The permissible limit of phenolic compounds in potable water is set up differently by various agencies, such as 0.001 mg/L by the Bureau of Indian Standards (BIS) [5], 0.001 mg/L by the World Health Organization (WHO) [6], and 0.1 mg/L by United States Environmental Protection Agency (USEPA) [7].

The removal of nitroaromatics from water resources is not an easy task because of their higher stability and solubility in water, and resistance to traditional water purification methods. In literature, numerous technologies have proposed eliminate been to nitroaromatics from aqueous medium. including the adsorption method. The adsorption process is one of the major methods for the removal of phenols, nitrophenols and some of their derivatives from aqueous solutions [8]. The adsorption method has some superior qualities compared to other methods, such as filtration, chemical precipitation and ion exchange, because it is easy to handle, easily regenerated by a suitable desorption process, insensitive to toxic pollutants and can be used for various situations without a large apparatus [9, 10]. In the adsorption process, several substances are used for water treatment, such as chemicals, biomass, carbon materials etc. [11 - 13]. Some adsorbents that were developed from low-cost materials by numerous chemical treatments include fertilizer waste [14], wood [15], rice husk [16], activated jute stick char [17]. carbon nanotubes [18, 19], activated carbon [20], zeolite [21] etc.. In recent years, the necessity for development of highly efficient, safe, cost effective environmentally benign and adsorbents for the elimination of contaminants including TNP from infected waters have gained greater interest of researchers across the world. Various low-cost biomass materials, such as tea waste, egg shell, rice husk, wheat straw, saw dust had revealed excellent sorption capacities for toxic pollutants from solution.

Nano-adsorbents have small size, higher surface area, easy separation, high reactivity and abundance of active sites for the removal of contaminants [22, 23].

polyaniline-(PANI)-based Currently, adsorbents received considerable have attention because of their low cost of synthesis. processability and easy environmental stability. Polyaniline is basically well-liked polymer because of its of synthesis, uniform conduction ease mechanism and superior environmental stability in the presence of oxygen and water [24]. It has various applications in the field of rechargeable batteries, electrochromic devices, photovoltaic chemical sensors. cells. electromagnetic interference (EMI) shielding, solar cells, anticorrosion coatings, sensors etc. [25, 26].

The doping of biomaterials into polyaniline generates advanced adsorbents, which show excellent efficiency, selectivity, and cost effectiveness, enhanced surface area, and provide a potential alternative to the conventional methods for the treatment of waste waters. Tea leaves are a fabulously network porous biomass material with structure, and their main dry matter are hemicelluloses, cellulose and lignin, condensed tannins, and structural proteins [27]. In earlier research studies it is confirmed that the tea leaves contain various functional groups, such as carboxyl, phenolic hydroxyl, and amine groups are also present [28, 29] and functionalities these have always been believed to effectively form some physicochemical interactions with water pollutants.

Therefore, the present study is focused on the fabrication of novel tea-waste-supported PANI composite (PANI-TWC) by loading of aniline onto tea waste biomass with the simultaneous adsorption and chemical oxidative polymerization of aniline and it was applied for effective removal of trinitrophenol (TNP) from aqueous medium in batch adsorption experiments. The influence of various factors, such as adsorbent dose, contact time, initial concentration and solution pH on the TNP removal capacity was tested. In order to understand the adsorption process and evaluate its performance, the experimental data were fitted with the Langmuir and Freundlich isotherms, and pseudo-first and pseudosecond-order kinetic models.

MATERIALS AND METHODS

Materials used

Aniline, hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium persulphate ($K_2S_2O_8$), ethyl alcohol (C_2H_5OH) and acetone (CH_3COCH_3) were purchased from Loba Chemicals. Trinitrophenol (TNP) was obtained from Fisher Scientific. All used chemical reagents were of analytical grade and used without further purification. The stock solution of trinitrophenol was prepared by dissolving 0.4 g of trinitrophenol in 1,000 mL of double distilled (DD) water. All aqueous solutions were prepared using deionized (DI) water.

Tea waste preparation

Tea waste biomass was collected from local tea shops after use in preparation of tea beverage and washed several times with deionized water and alcohol to remove impurity and soluble ingredient of tea leaves. After that, tea waste was dried for 2 h at 70 °C in hot air oven and cooled to room temperature. Dried tea waste was ground using pestle and mortar into fine powder and used for synthesis of PANI-tea waste (PANI-TWC) nanocomposite.

Synthesis of PANI-tea waste nanocomposite (PANI-TWC)

In the typical experiment, for the preparation of PANI-TWC, 2 mL of aniline was dissolved in 100 mL of 2M HCl with 1.0 g of tea waste powder and stirred for 2 h at room temperature. In a separate beaker, 0.25 M solution of $K_2S_2O_8$ was prepared in 100 mL of 2M HCl by dissolving 9.5 g and stirred for 30 min. After that, $K_2S_2O_8$ solution was added dropwise to the above mixture and stirred for 3 h at room temperature and kept overnight without any disturbance. After 24 h, the resulting dark green coloured PANI-TWC was filtered on a Whatman filter paper and washed several times with deionized water and ethanol to remove impurities and non-reacted aniline. Finally, the resulting PANI-TWC was washed with acetone and dried at 70 °C for 4 h in hot air oven. Furthermore, HCl doped polyaniline (PANI) was synthesized without mixing of tea waste powder using a similar procedure.

Adsorption experiments

The adsorption process of trinitrophenol (TNP) onto the PANI-TWC was conducted in aqueous medium at room temperature. The optimized conditions of experiment were achieved by varying solution pH, initial concentration of TNP, amount of dose of adsorbent and contact time. 100 mL of TNP solution with varied concentration of TNP (from 5 to 25 mg/L) was mixed with various amounts of the adsorbent dose (5 - 25 mg/100mL) and shaken for 5, 10, 15, 20, 25 and 30 min. The pH of the solutions was changed from 3 to 11 by the addition of either 0.1 M HCl or 0.1 M NaOH. An optimized amount of adsorbent of 15 mg was taken for all the adsorption experiments, except for dose optimization. The removal efficiency of TNP was calculated according to equation (1) [30]:

Removal efficiency =
$$\left(\frac{C_0 - C_e}{C_0}\right) \ge 100, \%$$
 (1)

where C_0 and C_e are the initial and equilibrium concentrations of TNP (mg/L) respectively. The equilibrium concentration of TNP was calculated according to equation (2) [31]:

$$q_{\rm e} = \left(\frac{C_{\rm i} - C_{\rm e}}{m}\right) V \tag{2}$$

where m is the mass of the adsorbent used (g), and V is the volume of solution used for adsorption (L).

Adsorption kinetic studies

To study the rate of adsorption of TNP onto the synthesized adsorbent, the kinetic study of the adsorption process was carried out. For this purpose, 100 mL solutions of TNP with 10 mg/L TNP each, taken in a 150 mL stoppered bottles with 15 mg of adsorbent amount at suitable pH and shaken in a shaker at room temperature (RT). Then the solutions were removed one by one at predetermined time intervals, centrifuged to remove adsorbent and analysed for residual TNP concentration using UV-visible spectrophotometer. To study the kinetics of adsorption, the adsorption data were simulated by the pseudo-first and pseudo-second-order kinetic models [32, 33]. The pseudo-first-order kinetic equation can be expressed by the following linear equation (3):

$$\log(q_{e} - q_{t}) = \log q_{e} - \left(\frac{k_{1}}{2.303}\right)t$$
(3)

where q_t (mg/g) is the amount of adsorbate adsorbed at time (*t*), k_1 is the first-order rate constant (min⁻¹). k_1 and q_e can be calculated from the slope and intercept of the plot drawn between $\ln(q_e - q_t)$ versus *t*. The pseudosecond-order kinetic equation can be illustrated by the following linear equation (4):

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 \, q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{4}$$

where k_2 (mg/g min) is the second order rate constant and q_e is the equilibrium adsorption capacity. k_2 and q_e can be determined experimentally by plotting graph between t/q_t versus *t*.

Adsorption isotherm studies

Isotherm models would be able to explain the distribution of adsorbate TNP between the solution and the PANI-TWC particles as well as the solute-solution interaction, and adsorption mechanisms [34]. The adsorption isotherm studies were carried out in batch experiments. For this study, 100 mL of TNP solutions with varied concentration of TNP (5 - 25 mg/L) were mixed with 15 mg constant

amount of adsorbent PANI-TWC, each taken in a 150 mL stoppered bottle, and shaken in a shaker for 30 min at room temperature at pH =6. The adsorbent was removed from the solution by centrifugation and solutions were analysed for residual concentration of TNP. The obtained experimental adsorption equilibrium data were analysed using the Langmuir [35, 36] and Freundlich [37, 38] isotherm models. The linear form of Langmuir isotherm is represented in equation (5):

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm max}K_{\rm L}} + \frac{C_{\rm e}}{q_{\rm max}}$$
(5)

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the adsorption capacity (amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent at equilibrium) (mg/g), q_{max} is the maximum mass of adsorbed adsorbate (mg/g). K_L (L/mg) is the Langmuir constant. The q_{max} and the K_L are calculated from the slope and intercept of the graph drawn between C_e/q_e vs. C_e . The linear form of Freundlich isotherm is expressed in equation (6):

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{\rm n} \log C_{\rm e} \tag{6}$$

where q_e is the amount of adsorbate adsorbed at equilibrium, K_F is the Freundlich constant and n is linearity constant. The plot of log q_e against log C_e gives a straight line, K_F and n values were determined from intercept and slope, respectively from a plot of log q_e against log C_e .

RESULTS AND DISCUSSION

Characterization PANI-tea nanocomposite

The functionalities present in the prepared PANI and PANI-TWC, and in tea waste powder were determined by using Fourier Transform Infrared Spectroscopy (FTIR) and UV-visible spectroscopy.

FTIR spectra

Polyaniline shows characteristic peaks at 1564 and 1481 cm⁻¹ attributing to the C=C stretching vibrations of the quinoid ring and the benzenoid ring, respectively, and C-N stretching vibration peaks for theses ring are observed at 1293 and 1105 cm⁻¹, respectively [39]. Figure 1a shows the FTIR spectra of pure PANI, tea waste and PANI-TWC. The appearance of a sharp peak in the range of 3400 - 3000 cm⁻¹ represents the stretching vibrations of the N-H bond in aromatic amines, the peak near 780 - 800 cm⁻¹ was assigned to the C-H out-of-plane bending vibrations, and the band near 1100 - 1130 cm⁻¹ is considered as a measure of the degree of electron delocalization in PANI chains and this is a characteristic peak related to PANI conductivity. In PANI-TWC sharp bands in the range of 3400 - 3000 cm⁻¹ related to amino group (N-H) are shifted at higher wave number values. The peaks observed at ~1570 and ~1470 cm⁻¹ for PANI are slightly shifted to higher wave number values, the band at ~1290 cm⁻¹ belongs to the C-N stretching vibration of the secondary aromatic amine strengthened by the protonation of PANI.

UV-visible spectroscopy

The UV-visible absorption spectrum of PANI shows broad bands at about 300 nm (due to the π - π * transition of the benzenoid ring of PANI), 370 nm (due to polaronic transition of PANI) and 680 nm (due to the bipolaronic transitions). The UV-visible absorption spectrum of PANI/tea waste nanocomposite shows two absorption maxima at 340 and 630 nm (Figure 1b). The band at 340 nm has been assigned to the p-p* electronic transition, this band is known to be sensitive to the number of aniline units. The excitation band at 630 nm can be used as a measure of the oxidation state of PANI which could be attributed to the standard emeraldine base.



Figure 1. a) FTIR and b) UV visible spectra of PANI and PANI-TWC

Batch adsorption studies of trinitrophenol (TNP)

Determination of dynamic adsorptiondesorption equilibrium

At the equilibrium in adsorption process, the rate of adsorption is equal to the rate of desorption. To achieve the dynamic adsorption-desorption equilibrium in the adsorption process of TNP onto PANI-TWC, batch experimental studies were carried out. A 100 mL of 10 mg/L TNP solution mixed with 15 mg adsorbent was shaken in 10 different stoppered bottles at optimized pH for 5 min to 50 min at room temperature. The bottles were removed one by one from shaker at predetermined reaction time and centrifuged to separate adsorbent. The residual concentration of TNP was quantified by UV-vis. absorption spectrum. The amount of adsorbate (q_t) adsorbed onto adsorbent PANI-TWC at various time periods was calculated using equation (2) and a graph shown in Figure 2 was plotted between q_t and contact time (t). From the graph it can be found that q_t is increasing up to 30 min of reaction time. However, after 30 min it becomes constant, hence at this point a dynamic adsorptiondesorption equilibrium has been achieved because the rate of absorption becomes equal to rate of desorption. Therefore, for this adsorption process, 30 min was considered as equilibrium time and same was applied for isotherm and kinetic studies.



Figure 2. Relation between q_t and contact time (t)

Effect of the contact time

The performance of the adsorption process is greatly affected by the contact time between the adsorbent and adsorbate. The process of adsorption started immediately within 5 min just after the addition of PANI-TWC to the TNP and the adsorption percentage increased with increasing contact time for any initial TNP concentration and achieved adsorptiondesorption equilibrium within 30 min. The experimental results indicated that almost 99 % of the TNP was removed within 30 min. The absorbance in UV visible spectra progressively decreased with time and nearly approached zero (Figure 3a) and the colour of the suspension changed from yellow to colourless within 30 min as shown in Figure 3b, which indicates the TNP was indeed adsorbed on the surface of PANI-TWC.



Figure 3. a) variation in absorbance intensity of TNP in UV visible spectra,b) decolourisation of TNP with time

Figure 4a shows the effect of the contact time on TNP removal from an aqueous solution with the PANI-TWC. At the initial stage of process, the higher rate of adsorption was observed which becomes slow with the passing time and finally it becomes constant because the increased amount of adsorbate on the surface of adsorbent covers the active sites on the adsorbent surfaces which resulted in a reduced adsorption rate.

Effect of pH on the TNP adsorption

pH plays significant role in the adsorption efficiency of the adsorbent. In order to study the effect of pH of solution on the adsorption of TNP onto PANI-TWC, the adsorption experiments were carried out at various pH values, i.e., from pH = 3 to pH = 11 with a 10 mg/L of TNP concentration taking 100 mL of solution and 15 mg of dose amount of adsorbent at room temperature for a 30 min equilibrium time.



Figure 4. Effect of contact time (a), pH of solution (b), dose of adsorbent (c) and initial concentration of trinitrophenol (TNP) (d) on adsorption of trinitrophenol (TNP) onto PANI-TWC

It can be seen from the results that the removal percentage of the TNP was decreased with the increase of pH value, as shown in Figure 4b. At lower pH, PANI-TWC adsorbent has a large number of positively charged polaron/bipolaron sites, which underwent electrostatic attraction with negatively charged pollutants. Therefore, the adsorption was higher at lower pH, while at higher pH value the positive charge on PANI-TWC decreased and, as a consequence, electrostatic repulsion nanocomposite between the and TNP increased. As a result, the adsorption rate of TNP decreased with increasing pH of solution.

In acidic pH or in presence of excess H^+ ion concentration, the solubility of TNP decreases, resulting in a decrease in adsorption of phenolic compounds since it is inversely proportional to solubility [40]. On the other hand, at higher pH, TNP generates picrate anion and the surface functional groups on the adsorbent become negatively charged, which keeping away the picrate anions and adsorption capacities decrease. Furthermore, the existence of stronger adsorbate-water bonds due to higher solubility of picrate anions in the aqueous solution also decreases the adsorption rate [41].

Dose optimization

To study the effect of various doses of the adsorbent on the rate of adsorption, the analysis was performed by varying the dose amount (5 mg, 10 mg, 15 mg and 20 mg respectively) and keeping both the pH of solution and the initial concentration of the TNP constant (100 mL of solution with 10 mg/L of TNP). The solutions were stirred for 30 min at room temperature. The following removal percentages of TNP were observed: 48 %, 75 %, 99 %, and 90 % for 5 mg, 10 mg, 15 mg, and 20 mg dose amounts, respectively, as shown in Figure 4c. The rate increase of TNP adsorption with the increase in the adsorbent dose is due to the more availability of active sites on the adsorbent surface for adsorption, and in the presence of a larger amount of adsorbent the adsorption percentage decreases due to overcrowding of particles, reduces the adsorbate-adsorbent which interactions to the attainment of equilibrium [42]. Therefore, a dose of 15 mg/100 mL (150 mg/L) was obtained as the optimized dose and used for the rest of the study.

Effects of initial TNP concentrations

In the adsorption process, the concentration of adsorbate is one of the important factors that influence the efficiency of adsorbent in aqueous medium. The effect of initial TNP concentrations on the elimination percentages of TNP by PANI-TWC is shown in Figure 4d. Approximately 90 % of TNP was removed at all initial concentrations of TNP. However, maximum removal performance (99 %) was observed at 10 mg/L initial concentration of TNP. Percentage removal of the TNP by the adsorbent increased when initial concentration was changed from 5 mg/L to 10 mg/L. However, further increase from 10 mg/L to 15 mg/L resulted in a decrease in TNP removal and the same happens with other initial increased concentration of TNP. Therefore, 10 mg/L concentration of the TNP was fixed as an optimized concentration of TNP for all experiments. The increased TNP concentration fully covered the available active sites on the adsorbent surfaces, which resulted in a decrease in the adsorption rate [43, 44].

Adsorption kinetics

Several models are available to investigate the adsorption kinetics mechanism, and the pseudo-first-order and pseudo-second-order reaction models are the most commonly applied among them. Here, the pseudo-firstorder and pseudo-second-order kinetic models were applied to fit the experimental data obtained from the batch experiments of the adsorption of the TNP onto the PANI-TWC adsorbent.

According to the pseudo-first-order kinetic model, the change in adsorbate concentration in solution must be proportional to time. It can be seen from the experimental data that the amount of TNP adsorbed on the surfaces of PANI-TWC increased for all studied reaction times and the percentage elimination of TNP also increased with rising of initial concentration. A significant difference is observed between the experimental value of q_e and the calculated value obtained from the linear plot, and the evaluated R² value of 0.943 (Table 1) is considered quite satisfactory, as shown in Figure 5a. These results suggest that the adsorption data are not well supported by the first-order kinetic model.

Table 1. Comparison of kinetic parameters for the adsorption of trinitrophenol (TNP) from solution onto PANI-TWC at pH = 6

Pseudo-first-order			Pseudo-second-order		
q_{e} (mg/g)	$k_1(\min^{-1})$	R ²	q _e (mg/g)	k ₂ (g/mg min)	R ²
37.0437	0.1260	0.943	66.7917	0.015545	0.997



Figure 5. Adsorption kinetic models for trinitrophenol (TNP) adsorption on PANI-TWC: a) pseudo-first-order, b) pseudo-second-order

The closeness of experimental q_e and theoretical q_e values and higher regression coefficient value ($\mathbb{R}^2 > 0.99$), as shown in Table 1 and Figure 5b, suggest that results of the adsorption of TNP onto the surfaces of PANI-TWC are well-fitted by the pseudo-second-order kinetic model. Thus, the adsorption follows pseudo-second-order kinetics.

Adsorption isotherms

The isotherm models are widely used to describe the adsorption processes, i.e., the Langmuir and Freundlich isotherms relate the rate of adsorption density (q_e) to the equilibrium TNP concentration in the bulk liquid phase (C_e). The Langmuir adsorption isotherm model suggests that the homogeneous surface and the adsorption of adsorbate take place by monolayer sorption without interaction among the adsorbate. The Freundlich isotherm describes the adsorption surfaces as heterogeneous and adsorption of assume monolayer adsorbate does not characteristics. The regression coefficient (R^2) indicating that the experimental values adsorption data are well fitted to linear form of Freundlich and Langmuir isotherm, as shown in Figure 6a and Figure 6b. However, Langmuir adsorption isotherm was found to be a favourable fit for the adsorption data. Value of regression coefficient (R^2) was 0.977, indicating a high degree of correlation between two variables. The predicted theoretical data of this model are summarized in Table 2.

Reuse of adsorbent

The stability and effectiveness of nanocomposite adsorbent materials is a crucial parameter for practical implication. In addition, reusability could be an emphasis on the cost-effectiveness of the process. The adsorbate was desorbed using acidic solutions, washed with water, dried and reused for the effective adsorption of TNP from aqueous samples in next five cycles. The percentage removal was effective in all cycles with slight decrease of activity of adsorbent.



Figure 6. Freundlich (a) and Langmuir (b) isotherm plot for the adsorption of various concentrations of trinitrophenol (TNP) from solution onto PANI-TWC

Table 2. Results of isotherm models for the	ıe
adsorption of trinitrophenol (TNP) from	L
solution onto PANI-TWC	

Langmuir isotherm			Freundlich isotherm		
$q_{ m max} \ (m mg/g)$	$K_{\rm L}$ (L mg ⁻¹)	\mathbb{R}^2	n	$K_{\rm F}({\rm mg/g})$	\mathbb{R}^2
224.4786	3.284	0.977	1.7168	206.764	0.94

CONCLUSION

The present adsorption study proves that environmentally hazardous trinitrophenol (TNP) can be efficiently remediated using PANI-TWC from aqueous media. Polyaniline itself is a good adsorbent for removal of negatively charged water pollutants, but the mixing of porous tea waste biomass increased the surface area and porous structure of adsorbent that further increased the adsorption rate of pollutant from aqueous media. The removal efficiency of trinitrophenol (TNP) was quick, and it was found to be strongly influenced by pH, contact time, dose of adsorbent. and initial concentration of adsorbate trinitrophenol (TNP). The maximum adsorption capacity was observed at pH = 3and equilibrium was achieved very quickly, 30 min. For adsorption isotherms, for Langmuir and Freundlich isotherm models were examined and model parameters were also determined. The overall experimental data were well fitted for Langmuir isotherm, indicating that adsorption surfaces are homogenous and mono-layered. The kinetics of adsorption was analysed by pseudo-first and pseudo-second-order kinetic models. It was found that pseudo-second-order kinetic model is better for the adsorption of trinitrophenol (TNP) by PANI-TWC.

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