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Nitrophenylfurfural grafted amino functionalized silica nanoparticles for adsorptive removal of tartrazine dye from water

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Abstract

In the present study, the synthesis of novel nitrophenylfurfural grafted silica nanoparticles (NPF-SiNPs) having multifunctional properties is reported. Using sol-gel process, the silica nanoparticles were functionalized with amino groups to develop amino functionalized silica nanoparticles (AFSi-NPs). Nitrophenylfurfural derivatives (para, ortho, meta) were further grafted onto AFSi-NPs surface to prepare the NPF-SiNPs using post grafting approach. X-ray Diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) were used for characterization of obtained AFSi-NPs, and NPF-SiNPs. The FTIR and XRD results revealed the occurrence of furfural derivatives on silica surface and BET analysis exposed a remarkable surface area of NPF-SiNPs especially when p-nitrophenylfurfural (80 m²/g) was used for modification of AFSi-NPs. TEM/SEM images depicted a spherical mesoporous morphology of as prepared NPF-
SiNPs having size 700-800 nm. The material (NPF-SiNPs) was then effectively applied for the adsorptive removal of tartrazine (TTZ) dye from wastewater. Out of three adsorbents ($p$-NPF-SiNPs, $o$-NPF-SiNPs, and $m$-NPF-SiNPs), the $p$-NPF-SiNPs showed higher activity towards TTZ removal. The influence of well-established adsorption parameters including pH, $p$-NPF-SiNPs dosage, temperature, TTZ concentration, and contact time were studied. Langmuir and Freundlich adsorption isotherm models were applied to simulate the equilibrium data. The equilibrium sorption data was better matched to the Langmuir isotherm model, as evidenced by the higher values of $r^2$ (near 1), which indicated the presence of an adsorption monolayer of TTZ on the surface of $p$-NPF-SiNPs. The maximum Langmuir adsorption capacity was found to be 203.5 mg/g at 323 K. The adsorption kinetic data for adsorption of TTZ onto $p$-NPF-SiNPs were correlated well to the pseudo-2nd (PS)-order model. In addition, TTZ adsorption process onto $p$-NPF-SiNPs was investigated on the molecular level using Monte Carlo and molecular dynamic simulations.

**Keywords:** Nitrophenylfurfural grafting; amino functionalized silica nanoparticles; adsorption; tartazine; kinetics.

1. Introduction

Various physical, chemical as well as biological processes, for example, coagulation-flocculation, biological methods, evaporation, oxidizing agents, pickering emulsions membrane technology, and photocatalysis have been employed for synthetic dyes removal form wastewater. Despite of being effective, these methods also present some setbacks in term of their sustainability in the long run [1-5]. Hence there is a need to broaden and exploit state-of-the-art technologies to deal with this menace. One such promising technology would be adsorption and among the various adsorbents used previously include mesoporous silica [6], modified silica [7], silica microspheres [8] activated alumina [9], activated carbon [10-12], activated clay [13], zeolites [14], metallic nanoparticles [15], and agricultural waste [16] etc. One of the most commonly utilized adsorbents for treatment of various pollutants is nano-silica. This is due to the facts that nano-silica has low toxicity, low cost, inorassociated high storage capacity, permeability, thermal and chemical stability, non-explosive nature, reusability after desorption and high porosity [17].

Monodisperse mesoporous silica nanoparticles (Si-NPs) are extensively used in various studies due to their unique structural properties including high surface area, large
pore size, biocompatibility and biodegradability, and stable water dispersibility. These properties made them suitable for wide range of applications in different fields of research and development [18-22]. One of the structural features of Si-NPs, being hydrophilic in nature, is to provide strong interaction with polar moieties through hydrogen bonding (present in the effluent stream). This hydrophilicity is accredited to the existence of number of silanol groups on the silica surface [23]. However hydrophilicity of Si-NPs could be tuned to high hydrophobicity, either through post modification or in-situ modification of the silica surface by various active functional groups as well as molecules [24]. This signifies that incorporation of suitable functional groups on silica surface increases the degree of adsorption of hydrophobic as well as hydrophilic moieties.

Ionic liquid modified silica nanoparticles and silane coupling agents ((R/O)\(_2\)SiR) have been extensively explored to change the silica surface in modified Si-NPs, which contain alkoxy silane monomers such as amine, chloro, methacryloxy, vinyl, glycidyloxy etc. [17, 25-27]. These organically modified Si-NPs find their application in the fields of adsorption [28], catalysis [29], biological applications [30], and enhanced oil recovery (EOR) etc. [31]. In present era, owing to the highly porous and stable nature of mesoporous Si-NPs, considerable attention has been drawn towards their adsorbent nature. It is established that morphology and surface characteristics have a great impact on adsorption performance. Excellent dye adsorption capacity is also associated with the samples having complex surface structure with large surface area, as much as interactive sites for organic pollutants are readily available [32].

This work aims to elucidate synthesis as well as characterization of amino functionalized silica nanoparticles (AFSi-NPs) and nitrophenylfurfurals grafted silica nanoparticles (NPF-SiNPs) and their application for the adsorptive removal of tartrazine (TTZ) dye from aqueous media. TTZ is a synthetic lemon-yellow azo dye that contains sulphonic acid. It is an important constituent of shells of medicinal capsules as well as hair products and is also used in food processing [33]. Azo dyes typically resist oxidation, ozone, biodegradation, temperature changes, and light [34]. Due to these important characteristics, dyes build in living things, which can cause serious illnesses and functional problems. TTZ is regarded as harmful to people because of its hyperactive effects, which can result in eczema, thyroid cancer, asthma, migraines, and other behavioral issues [35]. However, despite the breakthrough in the application of adsorptive technology in remedy of various organic pollutants, a through literature survey shows that the modification by grafting of
nitrophenylfurfurals onto silica network has not been reported till date and studies on the adsorptive removal of TTZ from wastewater using modified nanomaterials are rare.

However, in contrast to the reported materials, our synthesized material stands out due to its unique blend of multiple functionalities. Our aim was to create a hybrid material incorporating heterocyclic and homocyclic rings, alongside nitro and hydroxyl functional groups, an approach rarely encountered in existing materials. This pursuit was driven by the aspiration to engineer a material versatile enough for diverse applications. In our study, we focused on synthesizing this material to explore its potential in various applications. Initially, we conducted a wastewater treatment application taking TTZ as target pollutant to gauge its performance. Moreover, our investigation will extend to biomedical sensing as well as water splitting applications. Moving forward, we anticipate that this material holds promise for an array of applications, such as catalysis, energy storage, and sensing. Our preliminary assessments indicate its potential in these domains, prompting further exploration and in-depth studies to harness its capabilities.

So keeping this in mind, in the present study amino group was selected to modify the silica surface and in next step, this amino group assisted the chemical grafting of nitrophenylfurfurals on silica surface [34]. On the other hand, triphasic nature (aromatic, aldehyde and ethereal) of furfural [35] drawn author’s attention towards its grafting on nano-silica in order to enhance hydrophobic and hydrophilic characteristics of nano-silica. Furthermore, the affinities of nano-silica towards complex material were enhanced by fusion of nitrophenyl group with furfural prior to being grafted onto silica. Nitrophenyl group together with furfural ring have plenty of π-electronic cloud. Thus, the product synthesized by combination would be able to adsorb hydrophobic, hydrophilic as well complex moieties present in the media. AFSi-NPs and NPF-SiNPs were characterized using various techniques and applied for the adsorptive removal of TTZ from water. The effect of well-established parameters, for example, pH, mass of p-NPF-SiNPs, initial concentration of TTZ, and contact time were applied to evaluate the TTZ removal efficiency.

2. Materials and Methods

2.1. Chemicals

Chemicals used in the present study include furfural, tetraethoxysilane, p-nitroaniline, o-nitroaniline, m-nitroaniline, ammonia (NH3), cupric chloride (CuCl2), 3-aminopropyltriethoxysilane ((C2H5O)3Si(CH2)3NH2), sodium hydroxide (NaOH),
hexadecyltrimethylammonium chloride (C_{16}TMACl) and hydrochloric acid (HCl), which were obtained from Sigma-Aldrich (99% or higher) and were used after necessary purification process. The model dye TTZ was received as a kind gift from Stylers International, Lahore.

Scheme 1. (I) Synthesis of AFSi-NPs, (II) Synthesis of o/m/p-nitrophenylfurfural, and (III) Synthesis of NPF-SiNPs
2.2. Synthesis of NPF-SiNPs

Three steps were necessary to graft nitrophenylfurfurals onto the silica surface: (i) adding amino groups to the silica surface via an aqueous silane coupling reaction; (ii) making nitrophenylfurfurals; and (iii) using a simple condensation reaction heated at reflux to react the amino groups of silica and nitroarylurfural.

(i) Inclusion of amino group onto silica surface

AFSi-NPs were synthesized exercising the procedure reported by Suzuki using C$_{16}$TMACl as template under basic conditions [36]. A mixture of tetraethoxysilane (8.24 mmol) and 0.08 g of (C$_2$H$_5$O)$_3$Si(CH$_2$)$_3$NH$_2$ (0.43 mmol) were added to the methanol (50%) while stirring at 298 K for 8 h (Scheme 1-(I)). After 8 h, AFSi-NPs were separated from solution by filtration, washed with water, and dried at 318 K for 72 h. The white product was treated with concentrated HCl at 333 K to get rid of template molecules. The product was further filtered, subjected to several ethanol washings, and dried at 318 K. After that, the AFSi-NPs were treated with 1 mL of ammonia (28%) in order to remove any remaining Cl$^-$ ions.

(ii) Synthesis of nitrophenylfurfurals

Nitrophenylfurfurals were prepared using the procedure reported by Varshney [35]. For these reactions, freshly distilled furfural was treated with diazotized p/o/m-aromatic amines at a temperature range 0-5°C and CuCl$_2$ was used as a catalyst. After the reaction, the products were purified by steam distillation and recrystallization methods. The proposed reaction scheme of these reactions is represented in Scheme 1-(II).

(iii) Grafting of nitrophenylfurfurals on amine functionalized silica surface

To prepare NPF-SiNPs, 2 g of AFSi-NPs were mixed with equimolar amount of 5-nitrophenylfurfural in 25 mL of ethanol. The reaction mixture was heated under reflux for 2 h. After that the reaction mixture was cool down to room temperature and ice cold water was poured off into the reaction mixture and a solid product was filtered off, washed well with water. The product was dried in oven at 323 K. The general equation of these condensation reactions is presented in Scheme 1-(III).

By employing this general procedure, p/o/m-nitrophenylfurfurals were treated with AFSi-NPs separately. A Schiff based linkage was developed between the silica and furfural derivatives because reactive groups taking part in the reaction in each case were similar as aldehyde (-CHO) form nitrophenylfurfurals and amino (-NH$_2$) from AFSi-NPs. The chemical characteristics of these obtained products were similar to each other due to similar chemistry of these reactions and similar composition of reactants and products. However, there is a
difference in the reactivity of nitrophenylfurfurals due the different position of NO₂ group
and consequently it has effect on reaction rate and physical and chemical composition of the
products. These factors are explained in detail in section 3.2.7.

2.3. Characterization of nitrophenylfurfurals, AFSi-NPs and NPF-SiNPs
Nitrophenylfurfurals, AFSi-NPs and NPF-SiNPs were purified and characterized. GC-MS
and MS of nitrophenylfurfurals were recorded on GC-MS (Schimadzu QP2010) and mass
specrtrometer (MAT312 Model). Siemens D 5000 diffractometer with Cu-K radiation
(λ=1.54060 Å), at room temperature (298 K), was used to analyze the XRD patterns of AFSi-
NPs and NPF-SiNPs. Fourier transforms infrared (FTIR) spectroscopy of
nitrophenylfurfurals, AFSi-NPs and NPF-SiNPs was performed on Perkins Elmer FTIR
(spectrum RXI) spectrometer. FTIR spectra assisted to find changes in the functional groups
of pre and post grafted silica. SEM and TEM were used to analyses the surface morphology
and particle size of AFSi-NPs and NPF-SiNPs using (SEM Jeol, JSM-6390LA) and (JEOL
1010 TEM). The surfaces of synthesized materials were coated with gold by sputtering under
inert environment before the measurements. Using a TGA Universal Analyzer (2000 with
Universal V4.7A software), the thermal stability of AFSi-NPs and NPF-SiNPs was
investigated using thermogravimetric analysis (TGA). A Belsorp-mini II (BEL Japan) was
used to assess the N₂-adsorption-desorption isotherms at 323 K. Before measurement, the
sample was evacuated at 100°C under 103 mm Hg. Using adsorption data in the P/P₀ and
considering the linearity of a Brunauer-Emmett-Teller (BET) plot, the specific surface areas
were computed together with the pore diameters using the Barrett-Joyner-Halenda (BJH)
technique.

2.4. Batch adsorption studies
To examine the effects of well-known factors such pH, p-NPF-SiNPs dosage, agitation speed,
temperature, starting concentration of TTZ, and contact duration, TTZ adsorption study was
performed using a batch adsorption technique. Each solution was manually shaken using a
water bath shaker (Wisd, WiseShake SHO-2D, Seoul, South Korea) at a constant speed of
150 rpm. Once equilibrium had been reached, the samples were removed, and the solution
was filtered to remove the adsorbent. Using a double beam UV-Visible spectrophotometer,
the remaining concentration of TTZ in the supernatant was measured at 425 nm. Initial TTZ
concentration (20–120 mg/L), contact duration (5–90 minutes), pH variation (2–12), shaking
speed (50–200 rpm), temperature (303–323 K), and dosage (0.05–0.1 g/250 mL) of p-NPF–
SiNPs were some of the variables examined. The sample shaking duration of 90 min was
provided to reach equilibrium in all experiments. After the accomplishment of adsorption
process, the sample was filtered using ordinary filter paper. The quantity of TTZ adsorbed onto NPF-SiNPs and TTZ percentage removal were calculated using the equation S1 and S2 as presented in supplementary data (Section S1).

3. Results and Discussion

3.1. Characterization of synthesized nitrophenylfurfurals

In the FTIR spectra of o/m/p-nitrophenylfurfural as shown in Figure S1-S3 (supplementary data) stretching at ~3100 cm\(^{-1}\) was assigned to aromatic C-H and peak at ~2800 cm\(^{-1}\) was related to aliphatic C-H stretching. Another absorption peaks observed at around 1600 cm\(^{-1}\) allowed for the identification of the carbonyl group. The presence of NO\(_2\) in these compounds was indicated by peaks around ~1570 cm\(^{-1}\) and ~1500 cm\(^{-1}\) [37]. MS of purified o-nitrophenylfurfural (Figure S4) and GC-MS of m/p-nitrophenylfurfural were also obtained and presented in Figure S5, S6 (supplementary data). MS of o-nitrophenylfurfural exhibited a base peak at 217 related to its molecular weight. In the chromatogram of m-nitrophenylfurfural peak 2 showed maximum area and height as mentioned at the base of chromatogram. Database suggested a hit at a molecular weight of 217 with molecular formula C\(_{11}\)H\(_7\)NO\(_4\) that resembled 89% to the expected product m-nitrophenylfurfural. The peak 3 in the chromatogram of p-nitrophenylfurfural showed maximum area and height as mentioned at the base of chromatogram. The library suggested a hit at a molecular weight of 217 and molecular formula C\(_{11}\)H\(_7\)NO\(_4\) that resembled 92% to the expected product. The molecular ion peaks observed in mass fragmentations patterns of all the three products were at 190, which was also the base peak. The second peak at 171 was after the removal of NO\(_2\) group. The molecular mass of nitrobenzene, which corresponded to the second-highest peak at 115, demonstrated the breakdown of nitrobenzene from furfural [38]. p/o/m-nitrophenylfurfurals were further characterized by recording their melting points. The characteristic properties along with melting points of all the furfural derivatives synthesized during this study are presented in Table S1 (supplementary data). It can be observed that p-nitrophenylfurfural had higher melting point due to intermolecular hydrogen bonding which was not present in o-nitrophenylfurfural and m-nitrophenylfurfural. Due to intramolecular hydrogen bonding in o-nitrophenylfurfural, its modification on silica nanoparticles was poor compared to other derivatives. Further the m-nitrophenylfurfural had weaker acidic character compared to p-nitrophenylfurfural. Among the three nitrophenylfurfural, the p-nitrophenylfurfural had strong modification on silica nanoparticles. So due to this reason, p-nitrophenylfurfural was
further characterized. The $^1$HNMR spectrum of $p$-nitrophenylfurfural was conducted in DMSO and presented in Figure S7 (supplementary data). The types of H atom present in molecule and labelling of these protons are presented in Figure S8 and Section S2 (supplementary data) [38].

![Figure 1. XRD spectra of p-SiNPs, AFSi-NPs, and p/o/m-NPF-SiNPs](image)

**3.2. Characterization of AFSi-NPs and NPF-SiNPs**

3.2.1. XRD analysis of p-SiNPs, AFSi-NPs and NPF-SiNPs

XRD patterns of the pristine silica nanoparticles (p-SiNPs), AFSi-NPs and NPF-SiNPs are shown in Figure 1. It was observed that p-SiNPs exhibited a peak at 2θ value of 21.68 as can be seen in Figure 1 (green line) [36, 39], while in case of mesoporous silica the peak is...
shifted towards lower angles (20 value of \(\sim 10.2\)). AFSi-NPs and NPF-SiNPs showed a peak at a lower angle than 20 value of 22, which also suggested that these are mesoporous in nature [40]. Figure 1 (black line) represents the XRD pattern of AFSi-NPs having peak at 20 value of 12.38. Figure 1 (pink, blue, and red lines) shows diffused XRD peaks of \(p\), \(o\), and \(m\)-NPF-SiNPs respectively.

All these peaks had lower angles than normal silica with a slight difference in the intensity of curves. The height of intensity of peaks is in order \(m>o>p\)-NPF-SiNPs. This order is also reliant on the reactivity of reactants and most depression of peak at 11.40 was observed in case of \(p\)-nitrophentlfurfural which evident higher loading of para derivative and has further been explained in section 3.2.7. The decrease may possibly be due to the destruction of the crystal regularity in NPF-SiNPs as compared to pure silica. It was determined that the degree of meso-porosity had decreased in modified SiNPs. Overall XRD pattern is evidence of highest loading of \(p\)-nitrophenylfurfural on the surface of silica [36, 41].

![Figure 2. FTIR spectra of AFSi-NPs and \(p/o/m\)-NPF-SiNPs](image)

**3.2.2. FTIR analysis of AFSi-NPs and NPF-SiNPs**

FTIR spectra of AFSi-NPs and NPF-SiNPs are presented in Figure 2, which showed a remarkable peak at \(\sim 1050 \text{ cm}^{-1}\) and a bending peak at \(\sim 460 \text{ cm}^{-1}\) related to Si–O–Si
stretching and bending frequency respectively. These two peaks depicted that the backbone of structure is still composed of Si–O–Si network even after the modification reactions and grafting of organic moieties occurred purely on the amino groups present on silica surface [42]. It was observed that NPF-SiNPs demonstrated few additional peaks as compared to the AFSi-NPs. Two peaks found at 1674 cm$^{-1}$ and 1510 cm$^{-1}$ were linked to C=N and aromatic C=C stretching frequencies respectively. The silanol peak at 1639 cm$^{-1}$ (Figure 2a) had been replaced by carbonyl (C=O) peak at 1674 cm$^{-1}$ (Figure 2b, 2c, 2d). This indicated the occurrence of nitrophenylfurfural molecules on the exterior of AFSi-NPs. Further it also gave an indication that the $-\text{NH}_2$ group had reacted with $-\text{CHO}$ group of nitrophenylfurfural and had been converted to Schiff base (C=N$\equiv$). The peak observed at 3115 cm$^{-1}$ was linked to aromatic C-H stretching. Two peaks at 2948 cm$^{-1}$ and 2850 cm$^{-1}$ were assigned to the C-H stretching. Further the two peaks observed at 1367 cm$^{-1}$ 1245 cm$^{-1}$ were related the N-O C-N stretching frequencies respectively [43].

Figure 3. TEM images of $p$-NPF-SiNPs at low magnification (a) and high magnification (b)

3.2.3. Morphological study of AFSi-NPs and NPF-SiNPs

The morphology of AFSi-NPs and NPF-SiNPs was analyzed using SEM and TEM techniques. SEM images are shown in Figure S9 (supplementary data) and TEM images of $p$-NPF-SiNPs are presented in Figure 3. SEM image of AFSi-NPs in Figure S9a is presented for comparative analysis with NPF-SiNPs. Figure S9b represents the morphology of $o$-NPF-SiNPs. Image analysis showed that particle size had been increased ranging from 600-700 nm.
after grafting of nitroarylfurfural on AFSi-NPs. Figure S9c is the SEM image of \textit{m}-NPF-SiNPs. The reactivity of \textit{m}-nitroarylfurfural was less so most of the reactants were physically adsorbed onto each other and morphology of nanoparticles was irregular and size distribution was not very clear. Figure S9d is the SEM spectrograph of \textit{p}-NPF-SiNPs. It was clear from the image that there was a remarkable increment in the size of nanoparticles and size distribution was also more towards mono-dispersity. The size distribution ranged from 700-800 nm. TEM images of \textit{p}-NPF-SiNPs taken at low (Figure 3a) and high (Figure 3b) resolution further confirms the mono-dispersity of the nanoparticles. This behavior of morphology depends on the reactivity order of \textit{p/i/o}-nitroarylfurfurals, which has been explained in section 3.2.7.

3.2.4. Thermal characterization of \textit{p}-SiNPs, AFSi-NPs and NPF-SiNPs

TGA was used to ascertain thermal behaviour of pristine as well as modified SiNPs. The results of \textit{p}-SiNPs are presented in Figure S10 (supplementary data) whereas the results of modified SiNPs are shown in Figure 4 and Table S2 (supplementary data). Thermal analysis of \textit{p}-SiNPs exhibited an initial weight loss at 100°C related to evaporation water molecules and other solvent molecules moisture and a subsequent weight loss at 200°C followed by third weight loss above 200°C were linked to condensation of surface silanols and degradation of SiNPs, respectively [44]. Figure 4 demonstrates the TGA and DTG of AFSi-NPs and NPF-SiNPs. As can be seen from Figure 4A and 4B (black line) of TGA and DTG respectively, AFSi-NPs presented three decomposition stages. The initial stage (30–125°C) represented the evaporation of adsorbed water and carbon dioxide. The decomposition of aminopropyl groups started slowly at second step 125–380°C (37.4 wt%) followed by rapid decomposition above 380°C (9.6 wt%).

In contrast, \textit{o}-NPF-SiNPs showed four decomposition steps at 28–100°C (2 wt%), 100–250°C (6 wt%), 251-434°C (6.8 wt%) and 437-700°C (8%) as observed from TGA and DTG curves in Figure 4A and 4B (blue line). TGA and DTG curves (red lines in Figure 4A and 4B) of \textit{m}-NPF-SiNPs also showed four decomposition steps with a slight difference of temperature range as 28–120°C (4 wt%), 121–275°C (5 wt%), 276-46°C (7 wt%) and 447-700°C (9 wt%). The removal of adsorbed water and carbon dioxide is credited as being the initial step. Due to the nitro group's breakdown in the second phase, volatile molecules such as water, propenal, nitrogen, and nitrogen oxides were released. The breakdown of the phenyl and furan rings and the ether bond resulted in the production of ketone, 2-pentanone, and methyl isobutyl ketone in the third phase. The fourth phase was mostly attributable to the degradation of the propyl group into CO, H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{4}, and CH\textsubscript{4}.
Contrast to \( o/m \)-NPF-SiNPs, thermal decomposition curves of \( p \)-NPF-SiNPs had one additional decomposition step as shown by TGA and DTG curves in Fig. 4A and 4B (pink lines). This additional decomposition step may be evidence towards higher loading of \( p \)-nitrophenylfurfural onto AFSi-NPs. This trend of loading of nitrophenylfurfural onto AFSi-NPs is further explained in section 3.2.7. The description of decomposition steps was as 30–89\(^\circ\)C (2 wt%), 90–168\(^\circ\)C (5 wt%), 169–372\(^\circ\)C, 372–480\(^\circ\)C (6 wt%), and 481–700\(^\circ\)C (9 wt%). The removal of adsorbed water was cited as the initial stage. The second stage produced flammable substances including carbon dioxide and water. Due to the nitro group's breakdown in the third phase, propenal, nitrogen, and nitrogen oxides were produced. After the phenyl and furan rings and the ether connection were broken down in the fourth step, ketone, 2-pentanone, and methyl isobutyl ketone were formed. The breakdown of the propyl...
group was primarily responsible for the fifth step's release of CO, H$_2$O, C$_2$H$_4$, and CH$_4$.

3.2.5. Elemental analysis of AFSi-NPs and NPF-SiNPs

Table S3 (supplementary data) represents the elemental proportion (C, H and N) of AFSi-NPs and NPF-SiNPs. The study revealed that maximum loading of organic moities was achieved for $p$-NPF-SiNPs (C, 33.43%, H, 3.05%, N, 6.13%), followed by $o$-NPF-SiNPs (C, 48.58%, H, 2.84%, N, 5.42%), $m$-NPF-SiNPs (C, 22.86%, H, 4.44%, N, 8.463%) and AFSi-NPs (C, 3.54%, H, 2.13%, N, 0.42%). The nitrogen content observed for AFSi-NPs (∼0.42%) is trivial. The increase in nitrogen content was due to the presence of –NO$_2$ group in arylfurfurals. The extent of loading of arylfurfural on silica is explained in section 3.2.7 by theoretical assumption.

Figure 5. Adsorption/desorption isotherms of (A) $o$-NPF-SiNPs, (B) $m$-NPF-SiNPs and (C) $p$-NPF-SiNPs
3.2.6. BET analysis of p-SiNPs, AFSi-NPs and NPF-SiNPs

Information about surface area and pore size can be used to predict the adsorption capacity and behavior of p-SiNPs and organically modified SiNPs. The adsorption isotherms of p-SiNPs and modified SiNPs have been shown in Figure S11 (supplementary data) and 5 respectively. The isotherm of p-SiNPs exhibited three well defined stages as depicted in Figure S11. The initial stage at relative pressure ($P/P_0 = 0.1$) was related to the steady increase in nitrogen uptake and related to monolayer adsorption. The second stage found between 0.1 and 0.9 was linked to the capillary condensation process within the pores, and the third stage at higher $P/P_0$ (above 0.9) was linked to adsorption of gas in multilayer pattern on the external surface of the silica [45]. According to Figure 5, all samples with an adsorption isotherm had a substantially longer straight-line part of the curve. The longer the straight-line part of the curve in the low to moderate relative pressure range, the broader the range of pressures where monolayer adsorption dominates. Brunauer and Emmett's designation of point "B" as the initial point of the straight line indicated that the adsorption at that location was caused by the monolayer's capacity. However, when the pressure gradually increased, multi-layer of gas were developed on the surface of the adsorbent. In addition, the isotherms plot before capillary condensation showed no significant difference in the shape of the adsorbent surface and the amount adsorbed on the adsorbent surface.

At a relative pressure ($P/P_0$) of 0.61, threshold capillary condensation had been seen to generate a fast rise in the volume of the adsorbed quantity. As a result, there was maximum pressure ($P/P_0 = 1$) extremely close to the horizontal branch. At this stage the liquid had been absorbed into all of the pores. It has been noted that the sample with $p$-nitrophenylfurfural (Figure 5C) attained a saturation pressure within a very limited time as compared to the sample with $o$-nitrophenylfurfural (Figure 5A) and $m$-nitrophenylfurfural (Figure 5B). In addition, the abrupt jump above $P/P_0 = 0.9$ (in the case of B and C) typically presents the accomplishment of the monolayer adsorption. At this stage, the adsorption starts to progress beyond the monolayer to form multilayer adsorption. It helps to record the specific surface area of the material by analyzing the monolayer adsorption data before the multilayer adsorption begins. These claims are also in good agreement with the outcomes previously obtained from SEM analysis, as they also indicate that smale size particles have higher adsorption capacity. In general, high adsorption capacity is found in gases and very much linked to a large volume capacity (i.e. pore volume) and pore shape.

Surface area analysis is shown in Table S4 (supplementary data), and the results indicated that the specific surface area of the furfural grafted silica (NPF-SiNPs) as
determined by BET method was less than the specific surface area of AFSi-NPs. Further, p-NPF-SiNPs had the high surface area \((80 \text{ m}^2/\text{g})\) among all NPF-SiNPs \((47 \text{ m}^2/\text{g} \text{ for } o\text{-NPF-SiNPs} \text{ and } 21 \text{ m}^2/\text{g} \text{ for } m\text{-NPF-SiNPs})\). The less surface area of p-NPF-SiNPs \((80 \text{ m}^2/\text{g})\) as compared to AFSi-NPs \((148 \text{ m}^2/\text{g})\) is due to grafting of p-NPF on silica surface which cause pore blockage and result in reduced surface area as reported in our previous study [46]. The higher surface area of p-NPF-SiNPs as compared to o/m derivative is related to more reactivity p-nitrophenyl furfural. p-NPF chemically reacted with AFSi and caused less blockage of pores and has more surface area as compared to its other derivatives. The reduced surface area in case m-NPF-SiNPs and o-NPF-SiNPs may be attributed to less reactivity of o/m-NPF and their physical deposition on silica surface which cause pore blockage and hence reduced surface area.

Additionally, the pore volume and pore diameter p-NPF-SiNPs was also estimated by BJH model and found to be 0.721 cm\(^3\)/g and 18 nm (Table S4) [47].

3.2.7. Theoretical assumptions

It was observed from XRD, SEM, and TGA results that maximum loading occurred in p-NPF-SiNPs followed by o-NPF-SiNPs and m-NPF-SiNPs. This trend can be attributed to the resonance and inductive effect of –NO\(_2\) groups attached to aryl part of furfural. At o/p-positions these groups are more effective as compared to m-position. These –NO\(_2\) groups present at o/p-positions withdraw more electron density from the aryl and furfural rings and creates more positive charge on the carbonyl carbon of furfural and this C becomes more reactive as compared to m-nitrophenylfurufural. In addition, the presence of a nitro group at the ortho position typically induces distortion in the molecule, potentially leading to the existence of various resonance-contributing structures. In some cases, the nitrophenyl moiety may adopt a non-planar conformation, reducing its participation in resonance. Conversely, a nitro group at the meta position generally does not significantly engage in resonance phenomena. However, when the nitro group is positioned at the para position, it tends not to cause any distortion. Consequently, the nitrophenyl and furfural rings align coplanar, facilitating their full involvement in resonance. In this configuration, the nitro group withdraws electron density from the aldehyde group of furfurals, enhancing its reactivity. The arrows in Scheme 2 show the electron withdrawing trend of –NO\(_2\) group. In case of o/p-nitrophenylfurufural, it is easy for the amino group (–NH\(_2\)) of AFSi-NPs to attack the carbonyl C=O carbon and rate of reaction is increased, and result is more loading of arylfurfural on silica. In case of m-nitrophenylfurufural, –NO\(_2\) group does not facilitate to create positive
charge on carbonyl (C=O) carbon and rate of reaction becomes slow and there is less loading
of arylfurfural on silica.

\[ \text{Scheme 2. Electron withdrawing and loading trend of nitrophenylfurfurals} \]

### 3.3. Adsorptive study of TTZ onto NPF-SiNPs

The synthesis of Si-NPs grafted with nitrophenylfurfurals were achieved for the first-time
using condensation reaction. After characterization, the \( p \)-NPF-SiNPs, \( o \)-NPF-SiNPs and \( m \)-
NPF-SiNPs were used as adsorptive catalyst for the removal of TTZ from synthetic TTZ
solutions.

#### 3.3.1. Effect of pH and comparison of \( p \), \( o \), \( m \)-NPF-SiNPs for adsorption of TTZ

The initial screening experiment was performed using \( p \)-NPF-SiNPs, \( o \)-NPF-SiNPs and \( m \)-
NPF-SiNPs under different pHs to select the best adsorbent in terms of high adsorption
capacity for TTZ as well as the influence of pH ‘master variable’ of the solution on the
adsorption of TTZ. It is well known that the pH of the aqueous media plays a vital role in
controlling surface charge of the adsorbent, the degree of dissociation of the adsorbate as well
as activation of various functional groups on the active sites of the adsorbent [48]. The
adsorption study of TTZ was performed in pH range from 2 to 12 using 100 mL of 20 mg/L
TTZ solution and 20 mg of \( p/o/m \)-NPF-SiNPs. The data in Figure 6a show that the adsorptive
removal of TTZ onto \( p/o/m \)-NPF-SiNPs was highest at pH 4 and low at extreme acidic pH.
Further, when the pH was increased from 6 to 12, the adsorption capacities of \( p/o/m \)-NPF-
SiNPs decreased exponentially. This behavior can be explained in terms of ZPC of \( p/o/m \)-
NPF-SiNPs and existence of ionic form of the TTZ. The TTZ dye dissociates into as Dye-
\( \text{SO}_3^- \) and \( \text{Na}^+ \) ions in aqueous media ion having plenty of negatively charged surface. The
ZPC values were estimated and found between 4.5 and 6 for \( p/o/m \)-NPF-SiNPs (Figure 6b),
which indicated that surface of p/o/m-NPF-SiNPs was positive (NPF-SiNPs-OH+) when pH<pH_{ZPC} and negative (NPF-SiNPs-O^{-}) when pH>pH_{ZPC}.

Figure 6. Effect of pH on adsorption of TTZ onto p/o/m-NPF-SiNPs (a), and pH vs. ΔpH graphs of p/o/m-NPF-SiNPs (b)

The decrease in adsorption capacity at extreme acidic pH may be attributed to competition of H^{+} ions and positive surface of NPF-SiNPs. When the pH was increased to 4, the electrostatic interactions between NPF-SiNPs^{+} (ZPC=4.9-5.8) and Dye-SO_{3}^{-} increased due to low hydrogen ion (H^{+}) concentration resulting in highest adsorption of TTZ. Additionally non-polar interactions were also responsible for enhanced removal. The decrease in removal of TTZ under far acidic/neutral conditions is assumed due to decreased electrostatic forces between negatively charged NPF-SiNPs^{-} (ZPC=4.9-5.8) and Dye-SO_{3}^{-}. Further the exponential decrease at basic pH could be due to two factors; (1) very weak electrostatic forces or electrostatic repulsion between negatively charged NPF-SiNPs and TTZ (2) high concentration of OH^{-}, which can compete along with TTZ. Both conditions prevent the system from uptaking anionic dye. Moreover, variation in pH has an impact on the adsorptive process because it triggers the functional groups on the adsorbent surface to dissociate, which in turn tends to change the equilibrium conditions of the adsorption process.
Figure 6a also shows the comparison of all three adsorbents for the removal of TTZ. From Figure 6a, it can be seen that \( p \)-NPF-SiNPs had the highest adsorption capacity for TTZ adsorption. In this regard \( p \)-NPF-SiNPs were selected for further adsorption studies. The reason for the high efficiency of \( p \)-NPF-SiNPs and low efficiency of \( m \)-NPF-SiNPs was explained in section 3.2.7. Further, NPF-SiNPs have multi-functional groups having hydrophilic interior and hydrophobic exterior and contains nitrophenylfurfurals moiety with excess of \( \pi \)-electrons as presented in Scheme 3. Hence, NPF-SiNPs especially \( p \)-NPF-SiNPs have more capacity to trap and adsorb all three types of materials (hydrophilic, hydrophobic as well as complex organic and inorganic molecules) present in the aqueous media. In this case, the interactions between the sulphonic acid and hydroxyl groups of TTZ with the nitro and hydroxyl groups of NPF-SiNPs exhibit robust hydrogen bonding. Moreover, the phenyl and furfural groups within the structure display an affinity towards the phenyl groups present in TTZ, further contributing to the adsorption mechanism. These interactions collectively suggest a multifaceted binding scenario that enhances the effectiveness of NPF-SiNPs in capturing TTZ type pollutants as demonstrated in Scheme 3.

Scheme 3. Mechanism of micelle formation and TTZ interactions with NPF-SiNPs
Figure 7. Effect of agitation speed (A), p-NPF-SiNPs dose (B), and temperature (C) on adsorption of TTZ p-NPF-SiNPs

3.3.2. Effect of shaking speed

Shaking speed has a vital role in adsorption as it helps the dye molecules to cover the available adsorption sites provided by adsorbent in bulk solution. The effect of shaking speed was studied varying the shaking speed from 50 to 200 RPM after adding 20 mg of p-NPF-
SiNPs in 100 mL of 20 mg/L TTZ solution at pH 4. The results are presented in Figure 7A, which showed that the adsorptive removal of TTZ onto \( p \)-NPF-SiNPs was increased when shaking speed increased from 50 to 150 RPM and decreased with further increasing the shaking speed to 200 RPM. The maximum adsorption removal was found to be 97.85±2.1 mg/g at 150 RPM. The decrease in removal at high RPM may be due to desorption of TTZ from \( p \)-NPF-SiNPs.

### 3.3.3. Effect of p-NPF-SiNPs dosage

The amount of any adsorbent, which is correctly stated as g/L plays an active role in adsorption process. On TTZ removal, the effect of \( p \)-NPF-SiNPs dosage was investigated by varying the \( p \)-NPF-SiNPs dose from 0.02 to 0.04 g in 100 mL of 20 mg/L TTZ solution at pH 4 and results are shown in Figure 7B. The results revealed that the maximum adsorptive removal (92.12±2.6 mg/g) was achieved at 0.1 g and further increase in \( p \)-NPF-SiNPs dose resulted in low removal of TTZ. The decrease in adsorptive removal may be related to factors such as availability of adsorbent, electrostatic interaction between binding sites and reduced mixing due to high adsorbent concentration in the media. Therefore, due to the limited availability of adsorbates, many of the adsorption sites remain unsaturated, resulting in low adsorption efficiency. [49]. The results in Figure 7B also indicated that increasing the \( p \)-NPF-SiNPs dose up to 0.04 g had little effect on the adsorptive removal of TTZ.

### 3.3.4. Effect of temperature

Figure 7C illustrates the effect of temperature on the removal of TTZ onto \( p \)-NPF-SiNPs using 100 mL of 20 mg/L TTZ solution, 20 mg \( p \)-NPF-SiNPs dose and pH 4. From Figure 7C, it can be observed that rate of removal was increased with increasing the temperature from 303 to 323 K, suggesting the endothermic/chemical nature of adsorption process. The increase in removal may be attributed to the increase in the kinetic energy of the adsorbate (TTZ) with temperature, which enhanced the adsorbate availability at the active sites of the absorbent (\( p \)-NPF-SiNPs). In addition, increasing the solution temperature results in expansion of the pores and exposes more active sites within the adsorbent particles, which favors adsorption process [50].

### 3.4. Study of adsorption isotherms for TTZ removal onto \( p \)-NPF-SiNPs

For application of isotherm models, the experiments of initial TTZ concentrations were performed under three different temperature (303-323 K) using the following conditions (\( p \)-NPF-SiNPs dose 20 mg, volume of each TTZ solution 100 mL, pH 4, TTZ concentration 20-100 mg/L). In Figure S12 (supplementary data), the results of these experiments are presented, which revealed that the removal of TTZ increased with the increase of TTZ initial
concentration. Further it can be seen that the increase in temperature from 303 to 323 K resulted in slight increase of TTZ adsorption, a similar behavior as in Figure 7C. To examine the adsorption behavior and the level of interaction between $p$-NPF-SiNPs (adsorbent) and TTZ (adsorbate), the two most common isotherm models (Langmuir and Freundlich) were applied. A brief description and nonlinear equations of these models are provided in Section 3 (supplementary data).

The non-linear fitting was used to compute the parameters as well as the coefficient of determination ($r^2$) for both Langmuir and Freundlich models. The $b_L$, L/g (Langmuir rate constant) and $Q_{th}$, mg/g (theoretical adsorption capacity) were estimated from non-linear fitting of Langmuir model (Figure S13, supplementary data) whereas $K_F ((mg/g)(mg/L)^{1/n})$ and $1/n$ (adsorption intensity) were determined from non-linear fitting of Freundlich model (Figure S13, supplementary data). The calculated values of parameters and $r^2$ under 303 to 323 K are arranged in Table 1. The $r^2$ values obtained by fitting of Langmuir model (0.9793 to 0.9921) were higher compared to Freundlich model (0.9359 to 0.9525), which reflected that Langmuir model was well fitted to describe the mechanism of TTZ adsorption onto $p$-NPF-SiNPs at 303, 313, and 323 K. These results demonstrated that a monolayer adsorption was predominant on homogeneous surface of $p$-NPF-SiNPs. Additionally, the estimated values of $n$ (6.292 to 8.132) were less than 10, which is a clear indication of favorable adsorption of TTZ onto $p$-NPF-SiNPs. Besides, $q$ and $Q_{th}$ were in closeness also demonstrating favorable monolayer adsorption of TTZ onto $p$-NPF-SiNPs.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q$ (mg/g)</td>
<td>$Q_{th}$ (mg/g)</td>
</tr>
<tr>
<td>303</td>
<td>190.2</td>
<td>197.3</td>
</tr>
<tr>
<td>313</td>
<td>198.5</td>
<td>198.0</td>
</tr>
<tr>
<td>323</td>
<td>202.5</td>
<td>203.5</td>
</tr>
</tbody>
</table>

$q$ (Experimental adsorption capacity) = mg/g; $Q_{th}$ (Theoretical adsorption capacity) = mg/g; $b_L$ = L/mg; $K_F = [(mg g^{-1})(mg L^{-1})^{1/n}]$; RMSE = Root mean square deviation; $\chi^2$ = Chi square

To further confirm the validity of both models, the root mean square error (RMSE) and chi square ($\chi^2$) were calculated and presented in Table 1. The lower values of $\chi^2$ (1.432 to 4.289) and RMSE (6.371 to 9.905) for Langmuir model compared to Freundlich model ($\chi^2$ 10.68 to 15.08, RMSE 15.59 to 18.72) again confirmed the suitability of Langmuir model to explain the behavior of TTZ adsorption onto $p$-NPF-SiNPs.
3.5. Kinetics study for TTZ removal onto p-NPF-SiNPs

For application of kinetics models, the kinetic experiment was performed at three different TTZ concentrations (20, 40, 60 mg/L) in time range of 5 to 90 min by applying the following conditions (p-NPF-SiNPs dose 20 mg, volume of each TTZ solution 100 mL, pH 4). The results of these experiments are presented in Figure S12 (supplementary data). Figure S12 revealed that there was a linear increase in adsorption capacity of TTZ onto p-NPF-SiNPs when the time was increased from 5 to 25 min for all three concentrations, thereafter equilibrium was established, and no high removal rate was observed till 90 min. Various kinetic models have been developed to understand the adsorption process and have better description of rate controlling steps involved in adsorption. For the present study, the Lagergren pseudo-first (PF)-order and pseudo-second (PS)-order models as well as intraparticle-diffusion (ID)-model were selected to interpret the adsorption rate of TTZ onto p-NPF-SiNPs. The equations along with brief description of above-mentioned models are presented in Section 4 (supplementary data).

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TTZ conc. (mg/L) →</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Pseudo 1st order</td>
<td>q_t1 (mg/g)</td>
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</tr>
<tr>
<td></td>
<td>K_1 (1/min)</td>
<td>-0.0852</td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.6787</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.0748</td>
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<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>26.08</td>
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<tr>
<td></td>
<td></td>
<td>-0.0617</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8271</td>
</tr>
<tr>
<td>Experimental</td>
<td>q_t (mg/g)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>179.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>192.8</td>
</tr>
<tr>
<td>Pseudo 2nd order</td>
<td>q_t2 (mg/g)</td>
<td>93.46</td>
</tr>
<tr>
<td></td>
<td>K_2 (g/(mg min))</td>
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</tr>
<tr>
<td></td>
<td>r²</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>185.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0036</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9998</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>Region I K_i (mg/(g min^{0.5}))</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>10.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.87</td>
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<td>C</td>
<td>64.85</td>
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<td></td>
<td>121.7</td>
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<tr>
<td></td>
<td></td>
<td>134.9</td>
</tr>
<tr>
<td></td>
<td>Region II K_i (mg/(g min^{0.5}))</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.868</td>
</tr>
<tr>
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<td>171.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>189.1</td>
</tr>
</tbody>
</table>

The linear fitting was used to calculate the parameters as well as the coefficient of determination (r²) for both models. The PF-order constants, K_1 and q_t1 were estimated from slop and intercept of plot between log (q-q_t) vs t (Figure S14a) whereas the PS-order constants, K_2 and q_t2 were computed from intercept and slop of plot between t/q_t vs t (Figure
The calculated values of parameters and $r^2$ under 20, 40 and 60 mg/L TTZ were arranged in Table 2. The higher values of $r^2$ (0.9995 to 0.9998) from PS-order at all three TTZ concentrations indicated the best fitting of this model on data. Further the $q_t$ and $q_{t}$ values from PS-order model are in close agreement. Both these findings suggested that the PS-order model displayed a good fit to the experimental data obtained for TTZ adsorption onto $p$-NPF-SiNPs indicating chemical adsorption as rate limiting step. Moreover, the lower values of PS-order constant, $K_2$, (0.0081, 0.0036, 0.0042 for 20, 40, 60 mg/L TTZ) suggested smaller competition of surface sites for TTZ adsorption at low concentrations. Generally, the adsorption depends on both adsorbent and adsorbate involving chemisorption in addition to physisorption.

**Figure 8.** Application of ID-model on TTZ adsorption data using $p$-NPF-SiNPs

When TTZ in solution was mixed with $p$-NPF-SiNPs, the TTZ molecules are transported by diffusion into the pores of $p$-NPF-SiNPs through the interface between solution and adsorbent. This diffusion mechanism can be explained through ID-model, whose constants $K_i$ and $C$ were calculated from the slop and intercept of $q_t$ vs $t^{1/2}$ graph (Figure 8).
The values of ID-model are tabulated in Table 2. The plot $q_t$ vs $t^{1/2}$ is not linear instead it had two linear regions which indicated that other mechanisms were involved in addition to intraparticle diffusion. The first region indicated external surface adsorption/boundary layer effect where large amount of TTZ was rapidly adsorbed on exterior surface of $p$-NPF-SiNPs. The higher values of $C$ indicated the same predominant boundary effect. The second region illustrated slow TTZ adsorption onto $p$-NPF-SiNPs, which involved intraparticle or pore diffusion. Additionally, the linear line in ID-model plot did not pass through the origin which again confirmed that more than one process involved in TTZ adsorption.

3.6. Adsorption thermodynamics study

The effect of temperature on adsorption of TTZ onto $p$-NPF-SiNPs was appraised by performing adsorption experiments at (303, 313, and 323) K under optimized conditions ($p$-NPF-SiNPs dose 20 mg, volume of each TTZ solution 100 mL, pH 4). The results showed that when the temperature increased from 313 to 323 K, a slight increase in the adsorption capacity of $p$-NPF-SiNPs for TTZ removal was observed as shown in Figure S12 (supplementary data). The mounting adsorption tendency at higher temperatures depicted that the adsorption of TTZ followed the endothermic process suggesting a predominant chemisorption phenomenon.

**Table 3.** Thermodynamics parameters for TTZ adsorption onto $p$-NPF-SiNPs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>39.85±4.74</td>
</tr>
<tr>
<td>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>269.9±16.1</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol$^{-1}$)</td>
<td>303  -41.69±0.164</td>
</tr>
<tr>
<td></td>
<td>313  -45.12±0.257</td>
</tr>
<tr>
<td></td>
<td>323  -47.06±0.486</td>
</tr>
</tbody>
</table>

Obtained TTZ adsorption data at different temperatures was further used to find thermodynamic parameters such as enthalpy ($\Delta H$), entropy ($\Delta S$), and standard Gibb’s free energy ($\Delta G^\circ$) to endorse the feasibility, nature, and thermodynamic behavior of TTZ onto NPF-SiNPs. The thermodynamic parameters were computed using equations presented in Section 5 (supplementary data). The slope and intercept of plot $K_d$ vs. $1/T$ (Figure S15) were used to estimate the values of $\Delta H$ and $\Delta S$ respectively whereas equation S8 as presented in Section 5 (supplementary data) was applied to calculate the values of $\Delta G^\circ$. To make $K_d$
dimensionless, the Langmuir constant (L/mg) was first converted to L/mol and then these values were put in equation 1 as discussed in [51].

\[ K_d = \text{molecular weight of TTZ} \times 55.51 \text{ (mol/L)} \times b_L \times 1000 \]  \hspace{1cm} (1)

Where \( K_d \) is thermodynamic equilibrium constant. The calculated values of parameters are summarized in Table 3. The negative \( \Delta G^\circ \) values and an increase in negative \( \Delta G^\circ \) values with growing temperature is evidence that adsorption phenomenon is more favorable at higher temperatures. The positive value \( \Delta S \) as well as \( \Delta H \) showed that the adsorption of TTZ onto \( p\)-NPF-SiNPs is endothermic by nature and dominated by chemisorption [52, 53].

Table S5 displays a comparison of the adsorption uptake capacity of \( p\)-NPF-SiNPs for TTZ with other modified/unmodified materials. It is not obvious that \( p\)-NPF-SiNPs exhibited a higher and comparable affinity for TTZ as compared with majority of the modified adsorbents used for TTZ adsorption. This depicts the potential application of \( p\)-NPF-SiNPs as an efficient adsorbent for the removal of TTZ from contaminated wastewater as well as provides different ways to modify the nanomaterials with different organic entities to enhance the propertied of nanocatalysts.

3.7. Adsorption mechanism

TTZ adsorption process onto \( p\)-NPF-SiNPs was investigated on the molecular level using Monte Carlo and molecular dynamic simulations. Frenkel and Smit have provided descriptions of the fundamental ideas behind MC and MD simulations [54]. The \( p\)-NPF-SiNPs TTZ desorption sites were located using the MC simulation. The MD simulations of the MC's lowest-energy structures were carried out in explicit water to determine how the solvent molecules in the environment would affect the TTZ adsorption.

Figure 9a depicts the TTZ's dry solution surface adsorption on \( p\)-NPF-SiNPs (no solvent). Because \( p\)-NPF-SiNPs have several HB donor and acceptor sites, the TTZ molecule has created numerous hydrogen bonds with the hydroxide or -NH groups on its surface. The hydroxyl hydrogen atoms on the \( p\)-NPF-SiNPs surface interacted with the oxygen and nitrogen atoms of the amino group to generate HBs. In addition, hydroxyl hydrogen atoms, amine nitrogen atoms, and hydroxyl oxygen atoms with keto groups have been used to generate intramolecular HBs within TTZ. The adsorption of TTZ was analyzed using the two-layer model shown in Fig. 9b to determine whether TTZ can bind to the Si ions of the adsorbent. The Si ions have a variety of free connections in the two layers model. Si ions
with different free connections can be found at each sheet's edge. For instance, there are no free bonds, two free bonds, and three free bonds on metal ion-containing edges, respectively. Additionally, it was demonstrated that the functional groups of TTZ molecules create intramolecular hydrogen interactions with one another.

**Figure 9.** The lowest-energy configurations of the TTZ molecule on the $p$-NPF-SiNPs's surface in a dry condition (a, b) and MD images of the TTZ molecule being adsorbed on the $p$-NPF-SiNPs's surface in water (c, d). For clarity, the TTZ is presented in polyhedron form and the bond length is given in Angstroms.

Figure 9c depicts TTZ adsorption on the $p$-NPF-SiNPs, surface in the presence of water as well as MD snapshots for the two-layer models. The HO-Zn groups, keto, and
hydroxyl groups of the TTZ molecule form HBs when it adheres to the p-NPF-SiNPs surface in water (Figure 9c). The tertiary and primary amine groups do not generate HBs on the p-NPF-SiNPs surface. The coordination connections that the TTZ molecule made with Zn$^{2+}$ atoms in water are shown in Figure 9d. Both intramolecularly and intermolecularly between the functional groups of the TTZ molecule and the water molecules in both water systems, HBs were observed. In light of this, the MD simulations show that TTZ interacts with p-NPF-SiNPs even in the presence of water molecules [55].

4. Conclusion

Nitrophenylfurfural (a heterocyclic organic molecule) was successfully incorporated onto the AFSi-NPs to form hybrid, multifunctional, and narrow dispersed nanoparticles (NPF-SiNPs). XRD, FTIR, and TGA as well as Elemental analysis results revealed that the maximum loading of nitrophenylfurfural onto silica surface was observed in case of p-nitrophenylfural due to more reactivity in case of para substituent. The adsorption isotherm curves as revealed by BET results showed that all samples exhibited a noticeably long straight-line segment suggesting monolayer adsorption phenomenon domination, which further confirmed the completion of monolayer after modification (high surface 80 m$^2$/g for p-NPF-SiNPs). The particle size of the mono layer formed was between 600-750 nm before grafting and 700-850 nm after grating of p-nitrophenylfurfural as reflected by the SEM image signifying the presence of modified silica necessary for effective adsorption. Further study was conducted to determine the adsorptive potential of modified silica nanoparticles for adsorptive removal of TTZ from aqueous media. High surface area of p-NPF-SiNPs (80 m$^2$/g), with higher adsorption capacity was found due to the presence of multifunctional groups on it. The highest adsorption of TTZ onto p-NPF-SiNPs was found at pH 4, shaking speed of 150 rom, p-NPF-SiNPs dose of 0.1 g/0.5 L, and temperature 323 K. The maximum Langmuir adsorption capacity was estimated to be 203.5 mg/g at 323 K for TTZ removal by p-NPF-SiNPs. The adsorption process was followed by Langmuir and PS-order models. p-NPF-SiNPs, has three different types of functional characteristics. Its interior is hydrophilic, exterior is hydrophobic in nature, and contains nitrophenylfurfural moiety with excess of π-electrons. Hence, p-NPF-SiNPs have more capacity to trap and adsorb all three types of materials (Hydrophilic, hydrophobic as well as complex organic and inorganic molecules) present in the aqueous media. It can thus be concluded that the excellent adsorption
performance in case of TTZ reveals that as prepared multifunctional $p$-NPF-SiNPs have promising applications for efficient wastewater treatment.

**CRedit author statement**


**Declaration of competing interest**

The authors declare no competing interest.

**Acknowledgments**

We gratefully acknowledge Higher Education Commission Pakistan to support this work under the grant No. SRGP 1390. The authors extend their appreciation to the Researcher Supporting Project number (RSP2024R15), King Saud University Riyadh, Saudi Arabia. We are grateful for financial support from Chinese Academy of Sciences (CAS) President’s International Fellowship Initiative (PIFI) program for Visiting Scientists (Grant No. 2024PVB0003). MNZ acknowledges the CAS for the grant of “President’s International Fellowship Initiative (PIFI)” award.

**Supplementary data**

Figures S1 – S15, Tables S1 – S5, Sections S1 – S5

**References**


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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.