Adsorption of tobacco-specific nitrosamine 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone from aqueous solution with graphene aerogel

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Abstract. The adsorption behavior of graphene aerogel in the 4-(Methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) aqueous solution was studied. The adsorption kinetics fitted pseudo-second-order model with the rate constant ($k_2$) of 0.154 g/mg·h. The adsorption isotherm was investigated and fitted Langmuir and Freundlich models well, and the maximum adsorption capacity ($q_m$) was 59.66 mg/g estimated from Langmuir isotherm. Thermodynamic result indicated that the process of adsorption of NNK onto graphene aerogel was spontaneous and exothermic. Higher pH solution was favorable for NNK adsorption on graphene aerogel. The adsorption for NNK on graphene aerogel arose from the $\pi-\pi$ interaction between them, and the high adsorption efficiency was resulted from the -NO$_2$ functional groups. The capability of graphene aerogel was maintained after repeated absorption-desorption cycles, which was benefit for convenient separating and recycling of graphene aerogel.

1. Introduction

4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK), one carcinogenic tobacco alkaloid derivative, can cause tumors of the nasal mucosa, liver, and pancre to humans[1]. NNK is specifically formed in the tobacco and tobacco products. However, NNK was detected in source water and drinking water recently [2]. Thus, how to reduce the NNK in the environment water and wastewater is very important for the protection of the public health. Much efforts had been developed to reduce NNK in smoke and tobacco extracting solution by porous materials [3-5]. NNK could be adsorbed by zeolites by its N-N=O group inserted into the channels of adsorbent, and then catalytically degraded at high temperature by the fracture of N-NO bond. Moreover, incorporation of metal oxide in zeolites was able to further improve the adsorption and catalytic degradation of NNK [5].

In recent years, graphene, a novel 2D layered material, had received much scientific attentions with the great potential application in many fields. Among them, graphene showed excellent adsorption
capacity in the removal of heavy metal ions from aqueous solutions, dye pollutants, fluoride ions, etc. [6-8]. Comparing with other adsorbent, graphene exhibited the superiority of the selective adsorption ability to aromatic compound through strong π-π dispersion interaction. Consequently, graphene was expected to be a suitable adsorbent for the removal of pollutants with aromatic structures.

Aerogels was consisted of continuous nanopores forming open three dimensional networks, and in favour of providing effective mass transfer, which could further improve the adsorption behavior under suitable conditions [9,10]. Individual 2D graphene sheets were prone to stack in a parallel, resulting in the sacrifices of accessible surface area. However, 3D macroscopic assemblies could avoid the defect and exhibit better advantages, more paths with easy access and diffusion of ions and molecules could be provided in the application of catalysis, sensors, and so on. For this purpose, in this work, graphene aerogel was used as the adsorbent to remove NNK in aqueous solution. The adsorption capacity and behavior of graphene aerogels toward NNK, including adsorption kinetics, adsorption isotherms and thermodynamic parameters were systematically studied.

2. Experimental method
Graphite oxide (GO) was prepared by the modified Hummers’ method from the natural graphite with concentrated H2SO4 and KMnO4 as oxidant[11]. Typically, the graphene aerogel was prepared form GO suspensions with vitamin C as reducing agent. 100 mg of graphite oxide was added into 100 mL of distilled water to form homogeneous GO dispersion aqueous (2 mg/mL) under ultrasonic condition. Then, vitamin C was added to the dispersion with weight ratio of vitamin C to GO being 10:1. The dispersion was sealed in bottle and maintained at 95 °C for 2 h without stirring. The resulting sample was washed three times to remove impurities with water and ethanol and dried under vacuum condition.

The XRD patterns of the as-prepared sample were measured on a Bruker D8-advance powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Raman spectra were recorded with a HORIBA HR800 microscopic confocal spectrometer with a 514.5 nm argon laser. Field emission scanning electron micrographs of the as-prepared sample were observed on Hitachi SU-8010 field emission scanning electron microscope. Chemical compositions were analyzed with ULVAC-PHI, Quantera X-ray photoelectron spectroscopy (XPS). The charging effect was calibrated using the binding energy of C1s. Nitrogen adsorption/desorption was measured on a Micromeritics ASAP-2020 instrument at 77 K, the specific surface area of the samples was calculated by Brunauer-Emmett-Teller (BET) method.

Batch adsorption experiments were performed to evaluate the adsorption capacities of the graphene aerogel for NNK. The dependence of the initial solution concentration, solution pH, equilibration time and temperature dependent on NNK adsorption was investigated. 10 mg of graphene aerogel was added into 100 mL of NNK solution and shaken at room temperature with different NNK concentration (0.1-10 mg/L). The influence of pH in the range of 2-14 during the adsorption process was estimated with initial NNK concentration of 5 mg/L. The concentrations of NNK were determined on Spark Holland liquid chromatography coupled with TSQ Quantiva triple quadruple mass spectrometer.

3. Results and discussion
The XRD patterns of graphite and graphene aerogel was shown in Figure 1. As for the graphite, a sharp diffraction peak at 26.5° could be found which corresponded to the (d002) interlayer spacing
along the c-axis of 0.336 nm, disappeared in the graphene aerogel. The relatively weak and broad diffraction peak at 25.1° was the typical diffraction peak of graphene, corresponding to the (002) interlayer spacing of 0.353 nm. It could be seen that the interlayer spacing of graphene aerogel was slightly higher than that of graphite sample, indicating the presence of residual oxygen-containing groups in graphene aerogel and the existence of π–π stacking between graphene sheets [12]. Apparently, the broad XRD peak of graphene aerogel reflected that the graphene sheets along their stacking direction was the poor ordering, and the framework of graphene aerogel was composed of few-layer stacked graphene sheets.

**Figure 1.** XRD patterns of graphene aerogel.  
**Figure 2.** Raman spectra of graphene aerogel.

The Raman spectrum (514 nm excitation) of graphene aerogel sample was shown in Figure 2. As is shown, two Raman modes located at ca. 1350 and 1580 cm⁻¹ in the spectrum of the graphite sample was found, showing the existence of D band and G band. It was believed that G band corresponded to the E₂g mode for sp² graphitic carbon, and D band was associated with amorphous carbon indicating the existence of structural defects. Therefore, the intensity ratio of I_D/I_G could reflect the disorder degree in crystal structure. The low I_D/I_G value (0.04) of pure graphite indicated the existence of intact graphite domains. For the graphene aerogel, the intensity ratio of I_D/I_G increased to 1.41 which suggested localized disorder defects formed within sp² carbon network [13]. Based on the XRD and Raman results, it was conceivable that both highly disordered and randomly arranged graphene sheets existed in graphene aerogel.

The surface functional groups of obtained graphene aerogel were identified by XPS to provide the direct proof for the reduction of GO. The survey spectrum showed that the graphene aerogel contained C, O elements with the binding energy of about 532.1 and 284.2 eV respectively (figure 3a). The deconvoluted XPS peaks of C 1s exhibited the presence of four different carbon groups: the non-oxygenated C (C–C), the hydroxyl groups (C–OH), the carbonyl groups (C=O), and carboxyl groups (O=C–O) [14], with the binding energies of 284.7 eV, 286.4 eV, 288.2 eV and 289.1 eV, respectively (figure 3b). The XPS spectra confirmed that there were still some oxygen functional groups on the surface of graphene aerogel, arising from the incomplete reduction reaction of GO dispersion aqueous under the present conditions.
Figure 3. XPS spectra: (a) wide scan and (b) C1s spectra of graphene aerogel.

The morphological structure of graphene aerogel was characterized by SEM. The SEM images showed that graphene aerogel was composed of ultrathin graphene nanosheets with a porous structure to form well-defined and interconnected structure (figure 4a). The partial overlaps and wrinkles of thin film were the evidence of graphene nanosheets. The sizes of the thin film ranged from several hundreds of nanometers to micrometers (figure 4b). In the 3D macroscopic graphene aerogel, flexible dispersed graphene nanosheets were in contact with each other to form the network structure, and then increasing the bonding interactions. As a result, self-assembly occurred to form 3D architecture and porous structure in graphene aerogel, which was driven by the increased hydrophobicity, $\pi-\pi$ stacking interactions, and the cross-links between the remained oxygenated groups on the graphene sheets.

Figure 4. SEM images with different magnifications of graphene aerogel (a,b).

The specific surface area and porosity of the resulting graphene aerogel were revealed by nitrogen adsorption-desorption investigation (figure 5). The typical Type IV isotherm characteristic with adsorption hysteresis was observed in the adsorption-desorption isotherm of graphene aerogel, indicating the presence of mesoporosity. The pore size distribution curves suggested the presence of broad pores between 20 nm and 120 nm calculated from Barrett-Joyner-Halenda (BJH) model, which could be attributed to the interparticle pores from graphene sheets accumulation. It was worth mentioning that the specific surface area of the graphene aerogel was 133 m$^2$/g calculated from the Brunauer-Emmett-Teller (BET) method, which was lower than those of reported graphene aerogels. The relatively low specific surface area could be ascribed to the incomplete exfoliation and aggregation during the reduction reaction process.
Figure 5. BJH pore size distribution curve and N\textsubscript{2} adsorption-desorption isotherm (inset) of graphene aerogel.

The macroporous structure with open pores and large pore volumes endow aerogels with good absorbing properties. The adsorption kinetics of graphene aerogel was investigated by detecting the decrease of NNK concentration. Figure 6 showed the effect of contact time of NNK adsorbed by graphene aerogel. As was shown in figure 6, the adsorption capacity increased quickly and then reached the adsorption equilibrium within 2 h, suggesting that the adsorption process of NNK on graphene aerogel was not a constant speed and might be divided into two stages: fast stage and slow stage. For the first 2 h, up to 90\% of equilibrium absorption amounts of NNK in the solution were attained indicating most of the NNK molecule was absorbed to the surface of graphene aerogel at a fast rate because of the plenty of available adsorption sites on the graphene aerogel. There was no significant increase of adsorption capacity for graphene aerogel with the time prolonging to 4 h, which could be ascribed to the decrease of adsorption sites and the inhibition of absorbed NNK molecules with other molecules. The high adsorption rate at initial stages might be due to the existence of large number of adsorption sites, and then were saturated with the time prolonging. In addition, it was noticed that graphene aerogel floated on the surface of solution due to hydrophobic property during the absorption process. This property was important for the convenient separating and recycling of graphene aerogel.

The pseudo-second-order kinetics model was applied to analyze the kinetic adsorption of NNK on graphene aerogel. The pseudo-second-order model was described as [15]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e (\text{mg/g})\) is the amount of NNK absorbed at equilibrium; \(q_t (\text{mg/g})\) is the adsorption capacity at various time; \(k_2\) is the pseudo-second-order rate constant (g/mg·h). Therefore, the values of \(q_e\) and \(k_2\) were calculated from the slope and intercept of the linear plot of \(t/q_t\). The calculated kinetic constant (\(k_2\)) and correlation coefficient (\(R^2\)) were given in Figure 6. It can be seen that the adsorption kinetic constant for NNK adsorption on graphene aerogel was 0.154 g/mg·h, and the pseudo-second order model was properly fitted with a high \(R^2\) value of 0.989. Hence, the adsorption process of NNK on graphene aerogel could be described by the pseudo-second-order, implying the adsorption rate was depended on the concentration of adsorption sites of graphene aerogel. For the reason that external diffusion, adsorption, and internal particle diffusion were included in all the steps of adsorption for pseudo-second-order model, it could be concluded that the limiting step of adsorption rate was the chemisorption (i.e., valence forces) between graphene aerogel and NNK. The calculated adsorption amount (\(q_{e,cal}\)) of NNK on graphene aerogel obtained from the model was 11.53 mg/g, which was consistent with the experimental adsorption capacity (\(q_{e,exp}\)), implying that the adsorption for NNK...
was determined by graphene aerogel. Those results indicated that NNK uptake onto graphene aerogel was in accordance with the pseudo-second-order kinetic model.

\[ \frac{c_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L c_e} \]

Figure 6. Effect of contact time on the adsorption of NNK by graphene aerogel (10 mg of graphene aerogel and 100 mL of 1 mg/L NNK at 298.15 K, pH = 7).

The adsorption isotherm was obtained with different initial concentrations of NNK (0.1 to 10 mg/L). In the present work, Langmuir and Freundlich model were used to describe the adsorption equilibrium. The expression for the Langmuir model was as follows:

\[ \frac{c_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L c_e} \]

where \( c_e \) is the equilibrium concentration of NNK (mg/L); \( q_e \) is the adsorbed NNK amount on graphene aerogel (mg/g); \( q_m \) is Langmuir constant (maximum adsorption capacity, mg/g), it was assumed that monolayer coverage of the adsorption surface and no subsequent interaction among adsorbed substances in the Langmuir model, thus, \( q_m \) is corresponded to complete monolayer coverage; \( K_L \) is the Langmuir constant (L/mg), reflecting the affinity of the adsorbate with the adsorbent. \( A \) is obtained when \( q_m \) and \( K_L \) can be calculated from the straight line, which \( c_e/q_e \) was plotted against \( c_e \).

Freundlich model, an empirical model allowing for multilayer adsorption, was described as:

\[ \ln q_e = \frac{1}{n} \ln c_e + \ln K_F \]

\( K_F \) is the Freundlich adsorption constant, an indicator of the adsorption capacity; \( 1/n \) is an empirical parameter of adsorption intensity. \( 0<1/n<1 \) suggested favorable adsorption and the adsorption capacity increased and new adsorption sites form [16]. \( K_F \) and \( n \) can be calculated from the intercept and slope of the linear plot of \( q_e \) versus \( \ln c_e \).

The simulations of Langmuir and Freundlich isotherms at three different temperatures were shown in Figure 7. The adsorption capacity increased with the increasing equilibrium concentration of NNK and then reached equilibrium progressively, verifying the existence of surface diffusion and intra-particle diffusion in the adsorption process. Besides, the increase of NNK concentration could facilitate the diffusion of NNK molecules onto the graphene aerogel. The parameters of Langmuir and Freundlich adsorption isotherms of NNK on graphene aerogel at 298 K were given in Table 1. It was noticed that the correlation coefficient \( R^2 \) values were fitted both Langmuir and Freundlich isotherms well (\( R^2>0.97 \)). The Freundlich constant \( 1/n \) was between 0 and 1 for three temperatures, indicating that the adsorption was favorable under experimental conditions [16]. Moreover, the higher values of \( K_F \) at lower temperature indicated graphene aerogel possessed a higher adsorption capacity and affinity for NNK. The maximum adsorption capacity (\( q_m \)) at 298.15 K was determined to be 59.66 mg/g based on Langmuir model. It was approximately in a close agreement with the measured data. In
addition, \( q_m \) calculated from Langmuir model decreased with the temperature increasing, indicating that lower temperature was in favour of NNK adsorption, which was consistent with the result of Freundlich model. Based on the results, it could be concluded that both Langmuir and Freundlich isotherms agreed well with the experimental data.

![Figure 7](image_url)

**Figure 7.** Adsorption isotherms of NNK by graphene aerogel at three different temperature (10 mg graphene aerogel, 100 mL NNK, contact time 8 h, pH = 7). Langmuir model simulation (solid lines); Freundlich model simulation (the dotted lines).

| T(K)  | \( q_m \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) |
|-------|------------------|------------------|--------|---------|------|--------|
| 298.15| 59.66            | 3.0921           | 0.9826 | 38.8053 | 2.9314| 0.9858 |
| 318.15| 58.76            | 1.2230           | 0.9800 | 28.6449 | 2.1477| 0.9936 |
| 328.15| 55.04            | 0.8913           | 0.9783 | 23.9339 | 1.9792| 0.9965 |

To elucidate the NNK adsorption on graphene aerogel, the adsorption standard enthalpy change (\( \Delta H^\circ \)), standard entropy change (\( \Delta S^\circ \)) and free energy (\( \Delta G^\circ \)) were obtained from the adsorption of NNK by graphene aerogel at different temperatures. \( \Delta H^\circ \) and \( \Delta S^\circ \) reflected the adsorption process was endothermic or exothermic and spontaneous. The calculated value of \( \Delta H^\circ \) and \( \Delta S^\circ \) was -34.19 kJ/mol and -105.10 J/mol·K from the variation of the Langmuir constant (\( K_L \)), respectively (\( R^2 = 0.9921 \), as shown in table 2). According to the literature, the \( \Delta H^\circ \) value between 20.9 and 418.4 kJ/mol were commonly assumed to be associated with chemisorptions [17]. Hence, it was thought that NNK on graphene aerogel might proceed by chemisorption. The negative \( \Delta H^\circ \) value suggested the nature of adsorption was exothermic, supporting by the increase in the adsorption capacity of NNK with decline in temperature. Furthermore, the negative \( \Delta S^\circ \) indicated decreased randomness at the solid-liquid interface during the adsorption of NNK on graphene aerogel. The negative \( \Delta G^\circ \) (-2.86 kJ/mol at 298.15 K) suggested that the adsorption was a spontaneous process. In addition, the value of \( \Delta G^\circ \) became positive (0.29 kJ/mol) at 328.15 K, which indicated high temperature would prevent the adsorption of NNK on graphene aerogel.

| Thermodynamic constant | \( \Delta G^\circ \) (kJ/mol) | \( \Delta H^\circ \) (kJ/mol) | \( \Delta S^\circ \) (J/mol·K) |
|------------------------|-----------------------------|-----------------------------|-----------------------------|
| \( T(K) \)             | 298.15                      | 318.15                      | 328.15                      |
| \( 298.15 \)           | -2.86                       | -34.19                      | -105.10                     |
| \( 318.15 \)           | -0.76                       | -34.19                      | -105.10                     |
| \( 328.15 \)           | 0.29                        | -34.19                      | -105.10                     |

Table 2. Thermodynamic parameters of NNK adsorption on graphene aerogel.
The pH value was also one important factor to determine the adsorption behavior of an adsorbent, because it not only influenced the surface charge of the adsorbent, but also the degree of ionization of adsorbate\cite{18}. The results showed that the NNK molecule adsorption was strongly depended on the pH of solution, the adsorption capacity of graphene aerogel obviously increased in the pH range of 2.0 to 8.0. Further increasing pH from 8.0 to 14.0, the adsorption capacity of graphene aerogel slightly decreased and maintained stable for 40 mg/g at pH of 10.0. As reported, the reason for aromatic compounds adsorbed on graphene was originated from $\pi-\pi$ dispersion interaction between the aromatic ring electrons of adsorbate and those on the graphene plane \cite{19,20}. Considering that pyridine ring in the molecular structure of NNK were presented, we suggested $\pi-\pi$ interaction probably dominated the adsorption of NNK on graphene aerogel. Graphene aerogel was electrically neutral and presented a surface charge density close to zero over the whole pH value, which was proven by the zeta potential analysis. NNK was in molecular form in the basic pH range and started the protonation in around neutral range due to the pyridine ring in the molecular structure of NNK. Consequently, NNK was mostly ionized to mono-cation after protonation in acidic and neutral pH range, which weakened the $\pi-\pi$ interaction. Therefore, the reduction in adsorption capacity of graphene aerogel in acidic and neutral pH range was mainly owing to the weak $\pi-\pi$ dispersion interaction between ionized NNK and graphene aerogel.

The recycling performance for the NNK sorption capacity of graphene aerogel was evaluated and the six cycle experiments were performed. Under the same experimental condition, there was no evident decreasing for the adsorption capacity of graphene aerogel. Even after 6 cycles using methanol aqueous solution as eluent, more than 90% of the NNK sorption capacity can be preserved, exhibiting a good reliability for environmental pollutants adsorption. The efficient adsorption performance indicated that graphene aerogel possessed great potential in environmental treatment.

4. Conclusion
In this work, the adsorption of graphene aerogel for removing NNK from aqueous solution was demonstrated. The maximum adsorption capacity of graphene aerogel for NNK was 59.66 mg/g estimated from Langmuir isotherm. The kinetics data could be well fitted with the pseudo-second-order model. The isotherms data were fitted with both Langmuir and Freundlich equation. The high pH and low temperature were favorable for the adsorption. The adsorption mechanism of NNK on graphene aerogel was deduced to be via $\pi-\pi$ dispersion interaction. The pyridine ring in NNK molecular and hexagonal cells of the graphene aerogel facilitated $\pi-\pi$ dispersion interaction between them.

5. References
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