Oxidized g-C$_3$N$_4$/polyaniline nanofiber composite for the selective removal of hexavalent chromium

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Nanomaterials with selective adsorption properties are in demand for environmental applications. Herein, acid etching and oxidative decomposition of melon units of graphitic carbon nitride (g-C$_3$N$_4$) was performed to obtain the oxidized graphitic carbon nitride (Ox-g-C$_3$N$_4$) nanosheets. Ox-g-C$_3$N$_4$ nanosheets were further decorated on the polyaniline nanofiber (Ox-g-C$_3$N$_4$/Pani-NF). Ox-g-C$_3$N$_4$/Pani-NF was well characterized and further applied for a selective removal of hexavalent chromium (Cr(VI)) from aqueous solution. The zeta potential analysis indicate that the surface of Ox-g-C$_3$N$_4$/Pani-NF was positively charged which could be beneficial to bind anionic Cr(VI) ions electrostatically. In addition, nitrogen and oxygen containing functional groups exist on the Ox-g-C$_3$N$_4$/Pani-NF were mainly responsible for adsorption of Cr(VI) ions from aqueous solution. Moreover, the adsorption of Cr(VI) ions was also dependent on solution pH, reaction temperature and initial concentration of Cr(VI) ions. The maximum monolayer adsorption capacity of Ox-g-C$_3$N$_4$/Pani-NF for Cr(VI), calculated from Langmuir isotherm was 178.57 mg/g at pH = 2 and 30 °C. The activation energy ($E_a = -20.66$ kJ/mol) and the enthalpy change ($\Delta H^o = -22.055$ kJ/mol) validate the role of physical forces in adsorption of Cr(VI). These results demonstrate that Ox-g-C$_3$N$_4$/Pani-NF can be used as a potential adsorbent for environmental remediation applications.

The presence of hexavalent chromium (Cr(VI)) in wastewater is an exigent ecological problem due to its noxious property and amassing in the individual body throughout the food chain$^{1,2}$. To avoid the hazardous effect, Cr(VI) must be removed from wastewater to avoid any possible health and environmental risks. Various methods such as chemical oxidation/reduction, membrane filtration, ion-exchange, and adsorption/sorption have been explored for scavenging of heavy metals from aqueous solution and wastewater$^{1-9}$. Among the various methods, adsorptive separation and solid phase extraction have been considered as a capable technology for confiscation of heavy metals from contaminated water$^{14}$. The conventional (activated carbons, polymeric resins, clays) and non-conventional (agricultural and industrial wastes) materials have been reported to remove metallic pollutants from wastewaters$^{1,3-7}$. However, these materials have some intrinsic limitations like low sorption capacity, longer equilibrium time etc$^{6,7}$. Because of these reasons, novel adsorbents with exceptional high adsorption capacities and selective separation are necessary need.

Polymeric graphitic carbon nitride (g-C$_3$N$_4$) has been explored in environmental remediation, photocatalysis, organic photocatalysis, and in reduction of CO$_2$$^{10-15}$. The g-C$_3$N$_4$ is a low cost ecofriendly two-dimensional conjugated polymer that construct N-bridged “poly(tri-s-triazine)” to form graphitic plane (sp$^2$ hybridization) having van der Waals force interaction between the adjacent layers. The g-C$_3$N$_4$ has multiple defects, good chemical and thermally stable up to 600°C$^{11}$. One of the major advantages of g-C$_3$N$_4$ is that its electronic structure is tunable. Few articles published on adsorption properties of g-C$_3$N$_4$ shows its capacity for the removal of heavy metal. Shen et al.$^{16}$ used g-C$_3$N$_4$ for adsorption of Pb(II), Cu(II), Cd(II) and Ni(II). They observed that the adsorptive separation of metallic pollutants was possible through available nitrogen containing groups. Hu et al.$^{17}$ studied the adsorptive removal of aniline and Pb(II) onto the g-C$_3$N$_4$. The maximum sorption of Pb(II) and aniline onto the
g- C3N4 was possible at pH = 7 and 5. Anbia and Haqshenas18 synthesized the functionalized mesoporous g-C3N4 (surface area = 102.2 m²/g) for the adsorptive scavenging of Cu(II) and Pb(II). The maximum amount adsorbed was found to be 199.75 mg/g for Cu(II) and 196.34 mg/g for Pb(II), respectively. Thomas and Sandhyarani19 reported the fast adsorption of Cr(VI) onto g-C3N4-TiO2 mesoflowers from aqueous solution.

Various precursors such as melamine, urea, cyanamide and dicyanamide have been applied for the synthesis of g-C3N4 via a thermal condensation method16,17,19–21. Bulk g-C3N4 has the layered structure which is similar to the graphite. Due to the packed layered structure of g-C3N4, the active sites between the inter layers do not involve in adsorption process. Some strategies such as thermal chemical etching21,22 or ultrasound23 methods have applied to exfoliate and modify the layers of g-C3N4. Niu et al.21 reported that Hummers method is not suitable to form nanosheets and bulk g-C3N4 converts into nanosize particles. Li and coworkers had exfoliated and chemically oxidized bulk g-C3N4 using a mixture of K2Cr2O7 and H2SO4. Li and coworkers claimed that a mixture of K2Cr2O7 and H2SO4 could be efficiently used in exfoliation and oxidized bulk g-C3N4 into g-C3N4 nanosheets24. However, the complete separation of g-C3N4 nanosheets from aqueous solution could be challenging due to very small size like the graphene nanosheets, which might be cause nanotoxicity. To overcome this problem, g-C3N4 nanosheets can be decorated on the surface of other material which not only help in the recovery of g-C3N4 nanosheets but also enhance its adsorption capacity for metallic pollutants.

Polyaniline (Pani) and its composites have received more attention in few decades because of its easy synthesis, low cost and high adsorption capacity25,26. Pani can be easily synthesized by polymerization of aniline in acidic medium and the resulting Pani has net positive charge on its polymeric backbone which can interact electrostatically with the negatively charged Cr(VI)27,28. For instance, Bhaumik et al.27 synthesized polypyrrole-polyaniline nanofibers adsorbent for removal of Cr(VI) from aqueous solution. Zheng et al.28 prepared the Pani/Kapok fibers composite adsorbent to remove Cr(VI). By considering an easy synthesis of Pani and adsorption properties, it could be use to develop a new nanocomposite adsorbent with g-C3N4 nanosheets.

Herein, a ternary mixture of H2SO4-HNO3-H2O2 is used to exfoliate and oxidative alteration of bulk g-C3N4 into Ox-g-C3N4 nanosheets. The obtained Ox-g-C3N4 nanosheets are then decorated onto the Pani-NF to develop Ox-g-C3N4/Pani-NF composite synthesis. Previous studies reported that fibrous Pani has the large surface area compared to normal particles which may be better adsorbent. Thus in this work, the Pani fibers were prepared using soft template method. The crystal structure and chemical states of the synthesized materials have been studied in details. Adsorption studies in brief have further performed for the removal of Cr(VI) from aqueous solution.

### Results and Discussion

The strong π−π stacking among sp² carbon atoms is responsible for poor solubility, hydrophobicity and agglomeration of g-C3N4 nanosheets in various solvents. To overcome this problem, two strategies are applied: (i) introduction of hydrophilic groups on the g-C3N4 nanosheets and (ii) an auxiliary segregation of hydrophilic g-C3N4 nanosheets on polyaniline. Acid etching and oxidation process are applied to fabricate highly dispersible hydrophilic g-C3N4 nanosheets. It is reported in the literature that the oxygen containing functional groups along with defects in the materials can be created effectively using a mixture of strong acid and oxidizing agent at elevated temperature29,30. A schematic reaction route for an acid treatment of g-C3N4 nanosheets (Figure S1) and further synthesis of Ox-g-C3N4/Pani-NF composite is shown in Fig. 1. In this work, Pani-NF are synthesized through a soft template approach using ascorbic acid. Hydrogen bonding interactions play a vital role in an elongation of
Pani nanostructure. Ascorbic acid consists of four hydroxyl groups that are self-assembled by hydrogen bonding interactions and thus, a road-like structure is formed. The road-like self-assembled structure of ascorbic acid helps in the formation of self-assembled Pani-NF. However, ascorbic acid is a reducing agent and hinders the oxidative polymerization Pani-NF. Therefore, polymerization occurs slowly and completes in long time.

TEM analysis was carried out to observe the morphology of pristine g-C₃N₄; Ox-g-C₃N₄, Pani-NF and Ox-g-C₃N₄/Pani-NF composite. TEM image of bulk g-C₃N₄ exhibits solid agglomerates with a size of several micrometers (Figure S2a). It can be visualized from Figure S2b that the interconnected irregular small sheets like particles are obtained after acid-oxidative process. This TEM image confirms a successful reduction in size and alteration of pristine g-C₃N₄ nanosheets. Furthermore, a self-assembled ribbon-like morphology is appeared for pure Pani powder (Figure S2c). It is also observed that the interconnected small sheets of acid oxidized g-C₃N₄ decoration on Pani-NF (Figure 2). These results are revealing a successful synthesis of Ox-g-C₃N₄/Pani-NF composite.

The crystal and chemical structure of pristine g-C₃N₄, Ox-g-C₃N₄, Pani-NF and Ox-g-C₃N₄/Pani-NF composite are studied in detail using XRD, XPS and FTIR techniques. The XRD pattern of Pani-NF is presented in Figure 3. A wide peak ~25° validates an amorphous nature of Pani-NF. The XRD peaks for pristine g-C₃N₄ around 12.7° and 27.4°, corresponding to d spacing 0.693 and 0.324 nm are originated due to the interplanar structure packing of motif and carbon nitride interlayer stacking reflections. A slight variation in the XRD pattern of the acid-oxidized g-C₃N₄ (Ox-g-C₃N₄) nanosheets is observed. The intensity of the peak decreases and its position shifts from 27.42° to 28.2° due to the reduction in the gallery distance between the layers. Due to the chemical oxidation and etching, the oxidized g-C₃N₄ layers can be planarized by π–π stacking and H-bonding interactions. These interactions lead to the denser packing and reduction of the gallery distance between the layers. The intensity of the XRD peak for Ox-g-C₃N₄/Pani-NF composite is further reduced. This could be because of an interaction between Ox-g-C₃N₄ and Pani-NF. In addition, the characteristic peak for Pani is less pronounced in XRD pattern of Ox-g-C₃N₄/Pani-NF composite because Ox-g-C₃N₄ covered Pani-NF.

The introduction of oxygen-containing groups in Ox-g-C₃N₄ nanosheets after chemical modification is confirmed and analyzed through XPS study and the obtained results are presented in Figure 4. The atomic percentage...
obtained from XPS analysis in Ox-g-C₃N₄ for O 1s at 532.06 eV, N1s at 398.86 eV and C1s at 285.01 eV is 21.018, 23.955 and 55.028%, respectively. As shown in Fig. 4a, a strong peak at 532.06 eV for O 1s core level indicates the presence of oxygen containing groups in Ox-g-C₃N₄ nanosheets. Three peaks at 531.45, 532.16 and 533.47 eV after deconvolution of O 1s core level, are detected, which confirm the presence of carboxylic and hydroxyl groups. These peaks suggest that the oxygen containing groups are introduced on the surface after chemical treatment of g-C₃N₄ nanosheets. A slight variation in peaks position of oxygen species (O 1s) is appeared at 530.92, 531.93 and 533.31 eV for Ox-g-C₃N₄/Pani-NF composite (Fig. 4b). The C1s core level at 285.01 eV is deconvoluted into three main peaks centered at 285, 287.09 and 288.59 eV (Fig. 4c). These are attributed to graphitic sp² C=C bond, C-O bond and sp² hybridized C bonded to N in C-N=C-C coordination. Meanwhile, the peak position of C-C, C-O and C-N=C-N groups appeared at 285, 286.95 and 288.66 eV does not shows major shift in binding energy of C 1s core level for Ox-g-C₃N₄/Pani-NF composite (Fig. 4d). The N1s spectra (398.86 eV) of Ox-g-C₃N₄ also show three different peaks at around 398.68, 400.1 and 405.4 eV after deconvolution (Fig. 4e). These peaks are typically assigned to sp² bonded N atom in C-N=C-triazine rings, N-C₆ bridge atoms and π excitation in C≡N or uncondensed terminal amine groups. Three N 1 s peaks are also obtained in XPS spectrum of Ox-g-C₃N₄/Pani-NF composite (Fig. 4f) with slight changes in the peak position at 398.23, 399.89 and 404.85 eV. These results suggest that the chemical states of C, N and O in Ox-g-C₃N₄/Pani-NF are similar to Ox-g-C₃N₄.

FTIR spectra of pristine g-C₃N₄, Ox-g-C₃N₄, Pani-NF and Ox-g-C₃N₄/Pani-NF composite are shown in Fig. 5. A broad peak ~3000–3400 cm⁻¹ for pristine g-C₃N₄ nanosheets, is ascribed to the starching vibrations of primary and secondary amine groups. Moreover, broader and sharp peaks are observed for chemically oxidized g-C₃N₄ nanosheets. This is due to the introduction of oxygenous functional groups in modified g-C₃N₄ (Ox-g-C₃N₄) nanosheets. The adsorption bands at 807 and 880 cm⁻¹ are the characteristic peaks for tri-s-triazine units. The peaks at 1220–1450 cm⁻¹ are originated due to C-N stretching of aromatic rings and the peak at 1633 cm⁻¹ is attributed to the stretching vibrations of C≡N. After chemical etching, the peaks become more intense and sharp in Ox-g-C₃N₄, possibly due to the better-ordered packing of H-bond cohered long stand of polymeric melon units that left after chemical treatment. The characteristic absorption bands for Ox-g-C₃N₄/Pani-NF composite are similar to Ox-g-C₃N₄ and pure Pani-NF with a slight shift in their peak positions and intensities. The characteristic absorption bands for Ox-g-C₃N₄/Pani-NF composite are similar to Ox-g-C₃N₄ and pure Pani-NF with a slight shift in their peak positions and intensities. In Pani-NF spectrum, the characteristic peaks of benzenoid and quinoid rings occur at 1479 and 1550 cm⁻¹. The absorption bands at 1280 cm⁻¹ is ascribed to the C-N stretching vibrations. However, these absorption bands are shifted to 1286 cm⁻¹ in FTIR spectrum for Ox-g-C₃N₄/Pani-NF composite. The characteristic band at 790 cm⁻¹ is related to C-H vibration of aromatic ring plane and a slight variation in absorption band from 790 to 794 cm⁻¹ for aromatic C-H ring out plane is observed in FTIR spectrum of Ox-g-C₃N₄/Pani-NF composite. The

Figure 4. XPS analysis data for Ox-g-C₃N₄ and Ox-g-C₃N₄/Pani-NF composite, respectively. (a,b) O 1s (c,d) C 1s and (e,f) N 1s.

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significant shift in the characteristic bands of Ox-g-C3N4 and Pani-NF for Ox-g-C3N4/Pani-NF composite validate the interfacial interactions between Ox-g-C3N4 and Pani-NF.

The surface charge properties of pristine g-C3N4, Ox-g-C3N4, and Ox-g-C3N4/Pani-NF composite were evaluated using a zeta potential analyzer (Malvern, US). The obtained results are shown in Fig. 6a. The zeta potential and surface charge characteristics are increased with alteration in functionality of g-C3N4 (Fig. 6a). It is reported in the literature that the zeta potential of the stable nanomaterial is close to 30 mV. The zeta potential for Ox-g-C3N4/Pani-NF composite is found to be +21 mV, which validate its good dispersion and stability in compare with oxidized Ox-g-C3N4 (+19.2 mV) and pristine g-C3N4 (11.5 mV)40. The positive zeta potential values are attributed to the used of acidic condition for the modification and synthesis of g-C3N4 and Ox-g-C3N4/Pani-NF composites, respectively. The carboxyl and hydroxyl groups were created when a strong etching and oxidation of pristine g-C3N4 were simultaneously carried out using a ternary mixture of H2SO4, HNO3 and H2O2. Hence, the net positive charge on the surface of Ox-g-C3N4 is generated41. Similar protocol was used to synthesize Pani-NF and the decoration of Ox-g-C3N4 nanosheets onto Pani-NF in HCl solution. Amine and imine groups available in the Pani-NF backbone are prone to adsorb H+ from aqueous solution. Thus, a highly positively charged Ox-g-C3N4/Pani-NF composite is obtained. Overall, the synthesized Ox-g-C3N4/Pani-NF composite has ability to selective binding with the anionic Cr(VI) and a poor binding ability with positively charged Cu(II) owing to its net positive surface charge behavior, (Figure S3). Based on the primary metal adsorption study, Cr(VI) was chosen as a model pollutant to explore adsorption capacity of the synthesized materials.

The effect of adsorbent surface charge and Cr(VI) solution pH on the adsorption process are studied at the varied solution pH in the range from 2 to 9. The results are depicted in Fig. 6b, it can be seen that adsorption of Cr(VI) onto pristine g-C3N4, Ox-g-C3N4, and Ox-g-C3N4/Pani-NF composite increases sharply with decrease in solution pH. The optimum adsorption capacity is attained at pH 2. The solution pH not only influences the surface charge of the adsorbent, but also responsible for the speciation of Cr(VI) in aqueous solution. Cr(VI) exists in various stable forms like H2CrO4, HCrO4−, CrO42− and Cr2O72−, which is highly dependent on solution pH. HCrO4− is the main species of Cr(VI) at low pH, which can easily bind with the positively charged adsorbent
surface though electrostatic interactions. The adsorbent surface exhibits an amphoteric behavior with increase in solution pH, because the available functional groups (carboxyl, hydroxyl and amine) on the surface of adsorbents. At pH 1, Cr(VI) exists as $\text{H}_2\text{CrO}_4$ and $\text{HCrO}_4^-$, while at pH 2, Cr(VI) exists mostly as $\text{HCrO}_4^-$. The probability of $\text{H}_2\text{CrO}_4$ adsorption onto positively charged adsorbent surface is low compared to ionic $\text{HCrO}_4^-$ due to surface charge. Thus higher Cr(VI) adsorption is expected at pH 2. As the solution pH increases, positive charge on Ox-g-C$_3$N$_4$/Pani-NF composite surface reduces and the adsorption of Cr(VI) decreases with the increase in solution pH. A net negatively charged surface is developed on the adsorbent which shows an electrostatic repulsion with negatively charged Cr(VI) ions. The adsorption of Cr(VI) on the Ox-g-C$_3$N$_4$/Pani-NF composite is found to be much higher than the Ox-g-C$_3$N$_4$ and pristine g-C$_3$N$_4$ at all the studied pH. This can be attributed to the high positive zeta potential and the large number of surface functional groups (oxygenous and nitrogenous) present on Ox-g-C$_3$N$_4$/Pani-NF composite. Because of this reason, Ox-g-C$_3$N$_4$/Pani-NF composite is further explored for Cr(VI) adsorption at pH = 2.

Figure 7 shows the kinetics of Cr(VI) adsorption on the Ox-g-C$_3$N$_4$/Pani-NF composite at varied temperature. The adsorption of Cr(VI) increases with the increase in reaction time and equilibrium was established within 150 min. Moreover, reaction temperature also plays a positive impact to alleviate Cr(VI) by Ox-g-C$_3$N$_4$/Pani-NF composite. The adsorption capacity of Ox-g-C$_3$N$_4$/Pani-NF composite increases from 174.43 to 205.25 mg/g with increase in solution temperature from 30 to 50 °C, suggesting that adsorption process is endothermic in nature. To confirm the nature of Cr(VI) adsorption onto Ox-g-C$_3$N$_4$/Pani-NF composite, the data is fitted to the Gibbs and Van't Hoff equations.

$$\Delta G^\circ = -RT \ln K_c$$

where, $\Delta G^\circ$, $\Delta S^\circ$ and $\Delta H^\circ$ are the free energy change, entropy change, and enthalpy change, respectively. T, K and R are the reaction temperature (K), distribution coefficient and gas constant, (8.314 J/mol k), respectively. The obtained values of $\Delta G^\circ$ at 30, 40, and 50 °C are $-2.669$, $-3.054$, and $-4.307$ kJ/mol, indicating the spontaneous nature of adsorption process and the feasibility of Cr(VI) adsorption on the Ox-g-C$_3$N$_4$/Pani-NF composite. The values of $\Delta G^\circ$ ranges from $-20$ to $0$ kJ/mol and $-80$ to $-400$ kJ/mol are often for physisorption and chemisorption, respectively. In this study, the obtained $\Delta G^\circ$ values indicate that the adsorption of Cr(VI) onto Ox-g-C$_3$N$_4$/Pani-NF composite is physisorption. The positive value of $\Delta S$ (80.988 J/mol k) reflects an increase in randomness at the solid-solution interface via adsorption. Furthermore, the magnitude of $\Delta H^\circ$ also reflects an interaction between adsorbent (Ox-g-C$_3$N$_4$/Pani-NF) and adsorbate (Cr(VI)). The $\Delta H^\circ$ for chemisorption is usually between 40 and 120 kJ/mol, while the obtained $\Delta H^\circ$ value for Cr(VI) adsorption is 22.055 kJ/mol. Thus, the adsorptive removal of Cr(VI) by Ox-g-C$_3$N$_4$/Pani-NF composite is due to physisorption.

The experimental data presented in Fig. 7 is also fitted to the kinetic models to investigate the mechanism and rate controlling step occurs in Cr(VI) adsorption on the Ox-g-C$_3$N$_4$/Pani-NF. Pseudo-first order and pseudo-second order models are applied and equations of kinetics model, respectively, are:

$$\log(q_e - q) = \log q_e - k_t t/2.303$$

$$t/q_t = 1/k_2q_e^2 + t/q_e$$
where $q_e$ and $q_t$ are the adsorbed amount of Cr(VI) (mg/g) at equilibrium and time $t$ (min). $k_1$ and $k_2$ are the pseudo-first order (L/min) and pseudo-second order (g/mg min) rate constants. The plots for the pseudo-first order and pseudo-second order kinetic models are presented in Figure S4a,b and the rate constant values and the calculated equilibrium adsorption capacities, $q_{e,cal}$ (mg/g), for the pseudo-first order and pseudo-second order kinetic models are tabulated in Table 1. Pseudo-second order model is fitted well to the experimental data than the pseudo-first order kinetic data at all the temperatures studied because of high $R^2$ values. The calculated adsorption capacities of Ox-g-C$_3$N$_4$/Pani-NF composite for Cr(VI) adsorption as predicted from pseudo-second order kinetic model are much closer to the experimental adsorption capacity. This is confirming better fitting of the pseudo-second order kinetic model for adsorption process$^{50}$. Moreover, to find the activation energy ($E_a$) and type of adsorption forces, a linear relationship between the pseudo-second order rate constant ($k_2$) and temperature ($T$) is established using Arrhenius equation (5).

$$\ln k_2 = \ln k_0 - \left(\frac{E_a}{RT}\right)$$  

(5)

The magnitude of $E_a$ clarifies the forces involved in adsorption. The $E_a$ for physisorption varies between 5 to 40 kJ/mol and for chemisorption $E_a$ range from 40 to 800 kJ/mol. The $E_a$ for Cr(VI) adsorption on the Ox-g-C$_3$N$_4$/Pani-NF composite is 20.660 kJ/mol, indicating the involvement of physical forces in adsorption process$^{45}$. The impact of initial concentrations of Cr(VI) on the adsorption process is studied to find the maximum adsorption capacity and adsorption mechanism for Cr(VI) removal using Ox-g-C$_3$N$_4$/Pani-NF composite. As depicted in Fig. 8, adsorption capacity increases with initial concentration of Cr(VI) up to 200 mg/L, and thereafter adsorption reached to the plateau due to the saturation of available adsorption sites. The higher possibility of interaction between Cr(VI) and Ox-g-C$_3$N$_4$/Pani-NF composite at high initial concentration of Cr(VI) is that increase in the mass transfer driving forces$^{51}$. The equilibrium adsorption data presented in Fig. 8 is analyzed using Langmuir and Freundlich isotherm models. The Langmuir isotherm model is based on the monolayer coverage while the Freundlich isotherm model postulates an equilibrium on the heterogeneous adsorbent surface. The Langmuir equation can be represent as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \left(\frac{1}{b q_m}\right)$$  

(6)

where $q_m$ is the maximum monolayer adsorption capacity (mg/g) and $C_e$ is the Cr(VI) concentration at equilibrium (mg/L) and $b$ is a constant related to the energy of adsorption (L/mg). $q_m$ and $b$ are calculated from the slope and intercept of a linear plot of $C_e/q_e$ vs. $C_e$ (Figure S5a).

The Freundlich isotherm model can be represented as:

| Temp. °C | $q_{e,exp}$ (mg g$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $K_1$ (min$^{-1}$) | $R^2$ | $q_{e,cal}$ (mg/g) | $K_2$ (g/mg min) | $R^2$ |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 30      | 171.431         | 117.760         | 2.487 × 10$^{-2}$ | 0.954           | 181.185         | 4.044 × 10$^{-4}$ | 0.998           |
| 40      | 179.928         | 111.866         | 2.303 × 10$^{-2}$ | 0.960           | 196.078         | 3.941 × 10$^{-4}$ | 0.998           |
| 50      | 205.928         | 137.911         | 2.326 × 10$^{-2}$ | 0.989           | 217.391         | 3.265 × 10$^{-4}$ | 0.999           |

Table 1. Kinetics parameter for adsorption of Cr(VI) onto the Ox-g-C$_3$N$_4$/Pani-NF composite.

Figure 8. Effect of initial concentration of Cr(VI) on its adsorption onto Ox-g-C$_3$N$_4$/Pani-NF composite. (time- 210 min, temp. -30°C, pH-2.03, Vol. -25 ml, adsorbent mass- 0.015 g).
lnq_e = (1/n)lnC_e + lnK_F

(7)

where, q_e is the adsorption capacity at equilibrium (mg/g), K_F and n are constants that stands for the capacity and intensity, respectively. The parameters for Freundlich isotherm model are calculated from a plot of ln q_e vs. ln C_e (Figure S5b).

The calculated values of the Langmuir isotherm parameters q_m and b are 178.57 mg/g and 0.370 L/mg. On the other hand, the values of the Freundlich isotherm parameters n and K_F are 5.238 and 72.893 L/mg. It is noted that the correlation coefficient (R^2) value for the Freundlich isotherm is lower (0.7247) than that for the Langmuir isotherm (R^2–0.9986). This indicate that the Freundlich isotherm model is not suitable to describe Cr(VI) removal using Ox-g-C_3N_4/Pani-NF composite. The Langmuir isotherm model is much fitted well to the adsorption of Cr(VI) by Ox-g-C_3N_4/Pani-NF composite. Thus, adsorption behavior of Cr(VI) on the Ox-g-C_3N_4/Pani-NF composite seems to be monolayer and the possibility for interactions between adjacent Cr(VI) ions is negligible.\textsuperscript{51,52}

In addition, an essential feature of the Langmuir isotherm model is in term of dimensionless separation factor (R_L). For the favorable adsorption of Cr(VI) on the Ox-g-C_3N_4/Pani-NF composite, the R_L values must be in between 0 and 1. R_L > 1 and R_L = 0 indicate the unfavorable and irreversible adsorption process, respectively.\textsuperscript{53} The R_L can be defined as:

R_L = 1/(1 + b C_0)

(8)

where, C_0 is initial concentration of Cr(VI) (mg/L) and b is the Langmuir constant (L/mg). The R_L values obtained for Cr(VI) adsorption by Ox-g-C_3N_4/Pani-NF composite are in the range 0.097 and 0.010, which indicate the favorable adsorption process for Cr(VI), and the suitability of the Langmuir isotherm model for the adsorption equilibrium data.

To find the effectiveness of the synthesized material, the adsorption capacity of Ox-g-C_3N_4/Pani-NF composite has been compared with the previously reported adsorbents used for the removal of Cr(VI). The maximum monolayer adsorption capacities of various adsorbents and applied experimental conditions have been reported in Table 2. The results in Table 2 revealed that adsorption capacity of the adsorbents is highly dependent on the experimental conditions and used adsorbent. The adsorption capacity of Ox-g-C_3N_4/Pani-NF composite is comparatively higher than the previously reported adsorbents.

| Adsorbent                        | Adsorption capacity (mg/g) | pH  | Conc. (mg/L) | Vol. (ml) | Temp. (°C) | Time (h) | Dose (g) | Ref.    |
|----------------------------------|----------------------------|-----|--------------|-----------|------------|----------|----------|--------|
| Ox-g-C_3N_4/polyaniline-NF       | 178.57                     | 2   | 25–300       | 25        | 30         | 3        | 0.015    | This study |
| Rice husk                        | 31.1                       | 6   | 50–200       | 10        | 25         | 48       | 0.1      | 1      |
| Polyamine                        | 122.2                      | 4.5 | 100–400      | 25        | 30         | 3        | 0.05     | 28     |
| Kapok fiber/polyamine            | 60.65                      | 4.5 | —            | 25        | 30         | 3        | 0.05     | 28     |
| Fe_3O_4@SiO_2-mPD/SP             | 158.73                     | —   | 50–257       | —         | 30         | 24       | 1.0      | 42     |
| DBSA-Polyamine/MWCNTs            | 55.55                      | 2   | 20–140       | 15        | 30         | 10       | 0.02     | 49     |
| Bamboo charcoal grafted by Cr^{3+}-N-aminopropylsilane | 17.938   | 2–12 | 50–250   | 25        | 30         | 4        | 0.1      | 53     |
| Amino functionalized GO/Fe_3O_4  | 123.4                      | 2   | —            | —         | 20         | 12       | 0.2      | 43     |
| copper-benzenetricarboxylates    | 48                         | 7   | 10–40        | 10        | 25         | —        | 0.005    | 54     |
| polyamine/polygorskite           | 16.22                      | 5.5 | 2.5–35       | 40        | 35         | 24       | 0.02     | 55     |
| Longan seed activated carbon     | 169.49                     | 3   | 50–500       | 50        | 25.2       | 6        | 0.1      | 56     |

Table 2. The Maximum adsorption capacity of various adsorbents used for the removal of Cr(VI).
**Materials and Methods**

**Materials.** Aniline and oxidant potassium per-sulphate were obtained from BDH Ltd and SD Fine chemical Ltd, respectively. Sulphuric acid (98%), nitric acid (69%) and hydrogen peroxide were purchased from Panreac Quimica S.A.U. Melamine was obtained from Techno Pharmachem Haryana, India. Potassium dichromate, used for the preparation of Cr(VI) solution was provided by BDH chemical Ltd., Poole England.

**Oxidation of g-C3N4.** The g-C3N4 was prepared by thermal heating of melamine at 550 °C in a muffle furnace for 3 h at the heating rate of 5 °C/min. A yellow powder of g-C3N4 was obtained and thereafter, 2 g powder was added into 40 ml mixture solution of concentrated H2SO4 (98%) and HNO3 (69%) (1:1). The resulting mixture was heated at 40 °C under sonication for 2h and 3 ml H2O2 (33%) was then added dropwise and further sonicated for an additional 3 h for exfoliation. A whitish-yellow product was attained and 150 ml of deionized water was also added into the suspension. The dilute suspension of the oxidized g-C3N4 (Ox-g-C3N4) was centrifuged at 10000 rpm and washed alternatively with DI water, acetone and dried in oven at 70 °C for 12 h. Finally, the yellow colour exfoliated Ox-g-C3N4 sheets were obtained.

**Preparation of Ox-g-C3N4/polyaniline nanofibers composite.** Polyaniline nanofibers (Pani-NF) were initially synthesized by dissolving 0.88 g ascorbic acid in 100 ml HCl solution (1 M) and further stirred for 30 min. Then 1.6 ml aniline was added and stirred until a uniform solution obtained. Thereafter, the resulting solution was cooled in a refrigerator for 2 h and 100 ml of the cooled 0.1 M ammonium persulfate solution was added dropwise under continuous stirring. The polymerization was then allowed to extend transferring the solution in a refrigerator for 24 h without any agitation. The greenish product was obtained which was sonicated for 15 min and then stirred for 1 h. Afterwards, 0.5 g Ox-g-C3N4 suspended in 100 ml DI water using a sonicator for 2 h was added to polyaniline solution and further stirred for 24 h. The resulting precipitate was filtered, washed with DI water, acetone and dried in oven at 70 °C for 12 h to obtain Ox-g-C3N4@polyaniline nanofibers (Ox-g-C3N4/Pani-NF). Pani-NF was also synthesized by adopting a similar method without adding Ox-g-C3N4.

**Instrumentation.** The microstructure of g-C3N4, Ox-g-C3N4, Pani-NF, and Ox-g-C3N4/Pani-NF was examined by transmission electron microscopy (TEM) (model Tecnai G2 F20 Super Twin) at an accelerating voltage of 200 kV. Phase analysis was performed by X-ray diffractionmeter, Ultima-IV, Rigaku Corporation, Tokyo, Japan using Cu Kα radiation. The Fourier transform infrared (FTIR) spectra for g-C3N4, Ox-g-C3N4, Pani-NF, and Ox-g-C3N4/Pani-NF were recorded over a range of 400–4000 cm−1 using the Perkin Elmer Spectrum 100 FTIR Spectrometer. The chemical state and surface composition of Ox-g-C3N4 and Ox-g-C3N4/Pani-NF were analysed by X-ray photoelectron spectroscopic (XPS), SPECS GmbH, (Germany) spectrometer, using Mg-Kα(1253.6 eV X-ray source) at 13.5 kV, 150 W X-ray power.

**Adsorption of hexavalent chromium.** The adsorption of Cr(VI) was studied by mixing 0.015 g of the synthesized materials into 25 ml solution of metal ions stirring at 200 rpm in dark. The effect of solution pH was examined by varying solution pH in the range from 2 to 10 and the solution pH was adjusted using 0.1 M HCl or NaOH solution. The effect of initial Cr(VI) concentration was investigated at the varied concentrations from 25 to 300 mg/L at 30 °C. The equilibrium time studies were performed in a series of conical flasks agitated in the temperature range from 5 to 210 min at various temperature 30, 40 and 50 °C. After equilibrium attainment, the adsorbed amount of Cr(VI) by adsorbent was determined using a HACH curette test LCK313 reagent (Total chromium analysis). The adsorption capacity of the adsorbent was calculated in per unit mass of the adsorbent.

**References**

1. Ding, D., Ma, X., Shi, W., Lei, Z. & Zhang, Z. Insights into mechanisms of hexavalent chromium removal from aqueous solution by using rice husk pretreated using hydrothermal carbonization technology. *RSC Adv.* **6**, 74675–74682 (2016).
2. Chen, G., Feng, J., Wang, W., Yin, Y. & Liu, H. Photocatalytic removal of hexavalent chromium by newly designed and highly reductive TiO2 nanocrystals. *Water Res.* **108**, 383–390 (2017).
3. Wang, W., Wang, Z., Liu, J., Zhang, Z. & Sun, L. Single-step One-pot Synthesis of Graphene Foam/TiO2 Nanosheet Hybrids for Effective Water Treatment. *Sci. Rep.* **7**, 43755 (2017).
4. Kumar, R., Khan, M. A. & Haq, N. Application of carbon nanotubes in heavy metals remediation. *CRI. Rev. Environ. Sci. Technol.* **44**, 1000–1035 (2014).
5. Gupta, V. K., Carrott, P. J. M., Carrott M. M. L. R. & Suhas. Low cost adsorbents: Growing approach to wastewater treatment – A review. *CRI. Rev. Environ. Sci. Technol.* **39**, 783–842 (2009).
6. Zhong, Y. et al. Fabrication of Unique Magnetic Bionanocomposite for Highly Efficient Removal of Hexavalent Chromium from Water. *Sci. Rep.* **6**, 31090 (2016).
7. Dabrowski, A., Hubicki, Z., Podkościelny, P. & Robens, E. Selective removal of the heavy metal ions from waters and industrial wastewater by b ion-exchange method. *Chemosphere* **56**, 91–106 (2004).
8. Crini, G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **30**, 38–70 (2005).
9. Kumar, R., Kumar, M., Ahmad, R. & Barakat, M. A. L-methionine modified Dowex-50 ion-exchanger of reduced size for the separation and removal of Cu(II) and Ni(II) from aqueous solution. *Chem. Eng. J.* **218**, 32–38 (2013).
10. Ho, W. et al. Enhanced visible-light-driven photocatalytic removal of NO: Effect on layer distortion on g-C3N4 by H2 heating. *Appl. Catal. B: Environ.* **179**, 106–112 (2015).
11. Tan, L. et al. Synthesis of g-C3N4/CeO2 nanocomposites with improved catalytic activity on the thermal decomposition of ammonium perchlorate. *Appl. Surf. Sci.* **356**, 447–453 (2015).
12. Ansari, S. A. & Cho, M. H. Simple and large scale construction of MoS2/g-C3N4 heterostructures using mecanochemistry for high performance electrochemical supercapacitor and visible light photocatalytic applications. *Sci. Rep.* **7**, 43055 (2017).
13. Cao, S. & Yu, J. g-C₃N₄-based photocatalysts for hydrogen generation. J. Phys. Chem. Lett. 5, 2101–2107 (2014).
14. Schwinghammer, K. et al. Triazine-based carbon nitrides for visible-light-driven hydrogen evolution. Angew. Chem. Int. Ed. 52, 2435–2439 (2013).
15. Hong, J., Xia, X., Wang, Y. & Xu, R. Mesoporous carbon nitride with in situ sulfur doping for enhanced photocatalytic hydrogen evolution from water under visible light. J. Mater. Chem. 22, 15006–15012 (2012).
16. Shen, C. et al. Superior adsorption capacity of g-C₃N₄ for heavy metal ions from aqueous solutions. J. Colloid Interface Sci. 456, 7–14 (2015).
17. Hu, R. et al. Application of graphitic carbon nitride for the removal of Pb(II) and aniline from aqueous solutions. Chem. Eng. J. 260, 469–477 (2015).
18. Anbia, M. & Hajsadghasemi, M. Adsorption studies of Pb(II) and Cu(II) ions on mesoporous carbon nitride functionalized with melamine-based dendrimer amine. Int. J. Environ. Sci. Technol. 12, 2649–2664 (2015).
19. Thomas, T. R. & Sandhyarani, N. Template free synthesis of graphitic carbon nitride/titania mesoflowers. RSC Adv. 5, 72683–72690 (2015).
20. Liu, J., Zhang, T., Wang, Z., Dawsona, G. & Chen, W. Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity. J. Mater. Chem. 21, 14398–14401 (2011).
21. Niu, F., Zhang, L., Liu, G. & Cheng, H. M. Graphene-Like Carbon Nitride Nanosheets for Improved Photocatalytic Activities. Adv. Funct. Mater. 22, 4763–4770 (2012).
22. Sano, T. et al. Activation of graphitic carbon nitride (g-C₃N₄) by alkaline hydrothermal treatment for photocatalytic NO oxidation in gas phase. J. Mater. Chem. A 1, 6489–6496 (2013).
23. Zhang, X. et al. Enhanced photoresponsive ultrathin graphitic-phase C₃N₄ nanosheets for bioimaging. J. Am. Chem. Soc. 133, 18–21 (2011).
24. Li, H. J., Sun, B. W., Sui, L., Qiana, D. J. & Chen, M. Preparation of water-dispersible porous g-C₃N₄ with improved photocatalytic activity by chemical oxidation. Phys. Chem. Chem. Phys. 17, 3309–3315 (2015).
25. Khan, A. A. & Paquiza, L. Characterization and ion-exchange behavior of thermally stable nano-composite polyaniline zirconium titanate phosphate: Its analytical application in separation of toxic metals. Desalination 26, 242–254 (2011).
26. Morisi, R. E. & Elsabee, M. Z. Polyaniline Nanotubes: Mercury and competitive heavy metals uptake. RSC Adv. 5, 72683–72690 (2015).
27. Bhaumik, M., Maity, A., Srinivasu, V. V. & Onyango, M. S. Removal of hexavalent chromium from aqueous solution using polypyrrole-polyaniline nanofibers. Chem. Eng. J. 181–182, 323–333 (2012).
28. Zheng, Y., Wang, W., Huang, D. & Wang, A. Kapok fiber oriented–polyaniline nanofibers for efficient Cr(VI) removal. Chem. Eng. J. 191, 154–161 (2012).
29. Bu, X. et al. Surface Modification of C₃N₄ through Oxygen-Plasma Treatment: A Simple Way toward Excellent Hydrophilicity. ACS Appl. Mater. Interfaces 8, 31419–31425 (2016).
30. Cheng, F., Wang, H. & Dong, X. The amphoteric properties of g-C₃N₄ nanosheets and fabrication of their relevant heterostructure photocatalysts by an electrostatic re-assembly route. Chem. Commun. 51, 7176–7179 (2015).
31. Sk, M. M. & Yue, C. Y. Synthesis of polyaniline nanotubes using the self-assembly behaviour of vitamin C: a mechanistic study and application in electrochemical supercapacitors. J. Mater. Chem. A 2, 2830–2838 (2014).
32. Wu, W. et al. Facile fabrication of polyaniline nanotubes using the self-assembly behavior based on the hydrogen bonding: a mechanistic study and application in high-performance electrochemical supercapacitor electrode. Electrochim Acta 152, 126–134 (2015).
33. Wan, M. X. A template-free method towards conducting polymer nanostructures. Adv. Mater. 20, 2926–2932 (2008).
34. Dementjev, A. P. & X. Ray photoelectron spectroscopy reference data for identification of the C₃N₄ phase in carbon-nitrogen films. Diamond Relat. Mat. 9, 1904–1907 (2000).
35. Kim, M., Hwang, S. & Yu, J. S. Novel ordered nanoporous graphitic carbon nitride with C₃N₄ stoichiometry as a support for Pt-Ru anode catalyst in DMFC. J. Mater. Chem. 17, 1656–1659 (2007).
36. Dong, F. et al. In situ construction of g-C₃N₄/g-C₃N₄ metal-free heterojunction for enhanced visible-light photocatalysis. ACS Appl. Mater. Interfaces 5, 11392–11401 (2013).
37. Pandiselvi, K. et al. Constructing a novel carbon nitride/polyaniline/ZnO ternary heterostructure with enhanced photocatalytic performance using exfoliated carbon nitride nanosheets as supports. J. Hazard. Mat. 67, 67–77 (2016).
38. Zhu, Z. et al. Fabrication of conductive and high-dispersive Ppy@Ag@g-C₃N₄ composite photocatalysts for removing various pollutants in water. App. Surf. Sci. 387, 366–374 (2016).
39. Larkin, P. Infrared and Raman spectroscopy: principles and spectral interpretation, Academic Press, Elsevier, 2011.
40. Sun, H. et al. Novel core–shell magnetic nanogels synthesized in an emulsion-free aqueous system under UV irradiation for targeted radiopharmaceutical applications. J. Magnetism Magnetic Mat. 294, 273–280 (2005).
41. Wen, Z., Zhang, Y., Guo, S. & Chen, R. Facile template-free fabrication of iron manganese bimetal oxides nanospheres with excellent capability for heavy metals removal. J. Colloid Interface Sci. 486, 211–218 (2017).
42. Tan, L. et al. Multifunctional nanocomposite Fe₃O₄@SiO₂-mPD/SP for selective removal of Pb(II) and Cr(VI) from aqueous solutions. RSC Adv. 4, 45920–45929 (2014).
43. Zhao, D. et al. Facile preparation of amino functionalized grapheme oxide decorated with Fe₃O₄ nanospheres for the adsorption of Cr(VI). Adv. Surf. Sci. 384, 1–9 (2016).
44. Kara, A., Dемirbel, E., Tekin, N., Osmanu, B. & Basirli, N. Magnetic vinylphenylboronic acid microparticles for Cr(VI) adsorption: Kinetic, isotherm and thermodynamic studies. J. Hazard Mat. 286, 612–623 (2015).
45. Kwak, N. S., Yang, J. R., Hwang, C. W. & Hwang, T. S. The effect of a molecular weight and an amount of PEGDA (poly(ethylene glycol) diacrylate) on a preparation of sodium methallyl sulfonate-co-PEGDA microspheres and sorption behavior of Co(II). Chem. Eng. J. 223, 216–223 (2013).
46. Sun, Y. et al. Mechanistic insights into the decontamination of Th(IV) on graphene oxide-based composites by EXAFS and modeling techniques. Environ. Sci. Nano. https://doi.org/10.1039/C6EN00470A (2017).
47. Lagergren, S. Zur theorie der sogenannten adsorption gel oster stoffe. Kungliga Svenska Vetenskapsakademien. Handlingar, 25, 1–39 (1898).
48. Ho, Y. S. & McKay, G. Pseudo-second-order model for sorption processes. Process Biochem. 34, 451–466 (1999).
49. Kumar, R., Ansari, M. O. & Barakat, M. A. DBSA doped polyaniline/multi-walled carbon nanotubes composite for high efficiency removal of Cr(VI) from aqueous solution. Chem. Engineer. J. 228, 748–755 (2013).
50. Gheju, M., Balcu, I. & Mosea, G. Removal of Cr(VI) from aqueous solutions by adsorption on MnO₂. J. Hazard. Mat. 310, 270–277 (2016).
51. Gao, Y., Chen, C., Tan, X., Xu, H. & Zhu, K. Polyaniline-modified 3D-flower-like molybdhenium disulfide composite for efficient adsorption/photocatalytic reduction of Cr(VI). J. Colloid Interface Sci. 476, 62–70 (2016).
52. Namisaywam, C. & Kavita, D. Removal of Congo red from water by adsorption on to activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigm. 54, 47–58 (2002).
53. Wu, Y. et al. Adsorption of hexavalent chromium onto Bamboo Charcoal grafted by Cu²⁺–N-aminopropylsilane complexes: Optimization, kinetic, and isotherm studies. J. Ind. Eng. Chem. 46, 222–233 (2017).
54. Maleki, A., Hayati, B., Naghizadeh, M. & Joo, S. W. Adsorption of hexavalent chromium by metal organic frameworks from aqueous solution. *J. Ind. Eng. Chem.* **28**, 211–216 (2015).

55. Wang, J., Han, X., Ji, Y. & Ma, H. Adsorption of Cr(VI) from aqueous solution onto short-chain polyaniline/palygorskite composites. *Desalin Water Treat.* **56**, 356–365 (2015).

56. Yang, J., Yu, M. & Chen, W. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from longan seed: Kinetics, equilibrium and thermodynamics. *J. Ind. Eng. Chem.* **21**, 414–422 (2015).

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**Author Contributions**

R.K., M.A.B. and F.A.A. designed experiments and wrote the manuscript. R.K. performed the experiments. All the authors reviewed the manuscript.

**Additional Information**

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