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# Paper Title

Enhanced Cr(VI) Adsorption on Nitrogen and Sulfur Functionalized Granular Activated Carbon

## Authors

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## Abstract

The effect of functionalizing a granular activated carbon (GAC) adsorbent with nitrogen and sulfur groups was investigated, with the aim of enhancing the adsorption capacity for hexavalent chromium (Cr(VI)) from aqueous solutions. The modification of GAC with nitrogen and sulfur groups was achieved in a one pot hydrothermal process using thiourea as the precursor. The amount of nitrogen and sulfur incorporated onto the GAC using this process were 1.6% and 1.0% based on XPS analysis, and 0.72 at.% and 1.22 at.% based on CHNS analysis, respectively. The modified GAC exhibited higher adsorption capacity compared with the unmodified GAC across all tested pH levels and ionic strengths with highest value of 23.2 mg/g at pH 3, compared with 20.5 mg/g for the unmodified GAC. The N/S functionalized GAC favored the reduction of Cr(VI) to Cr(III) during the adsorption process, which is considered to have lower toxicity. XPS and FTIR analyses, together with desorption experiments, suggest that adsorption primarily occurs through hydrogen bonding and reduction-adsorption mechanisms for N/S functionalized GAC. Isotherm analysis revealed that Cr(VI) adsorbs predominantly as a monolayer of  $\text{HCrO}_4^-$  on the heterogeneous GAC surface (Sips model), whereas N/S-functionalized GAC follows the Freundlich model, indicating heterogeneous adsorption through the formation of Cr(III) hydroxides near



functional groups. Kinetic studies indicated that the adsorption follows a revised pseudo-second order kinetic model on both surfaces, where chemisorption is the rate-controlling step. The rate of adsorption is similar for both types of GAC in the initial regime with fast kinetics. However, after 200 min, N/S functionalized GAC exhibits a higher uptake, likely associated with the additional Cr(VI) adsorption through a reduction process. Regeneration experiments revealed that NaOH and KOH solutions achieved significantly higher desorption efficiencies (>90% for unmodified GAC and >70% for N/S functionalized GAC) compared to an acidic regeneration using HCl solution (<40% for GAC and <25% for N/S-GAC).

## Keywords:

Granular activated carbon (GAC), Surface modification, nitrogen and sulfur functional groups, Adsorption mechanism. Reduction-adsorption, Cr(VI), Cr(III).

## 1. Introduction

Heavy metals are commonly used in numerous industries such as metal plating, battery manufacturing, and tanneries. The wastewater produced from these industries has high concentrations of metal ions which can pose severe health problems for humans and animals.<sup>1,2</sup> Among heavy metals, chromium, among heavy metals, is associated with particularly high health hazards.<sup>3</sup> Chromium from industrial effluents mainly exists in two oxidation states: trivalent chromium Cr (III), and hexavalent chromium Cr(VI). The latter is much more toxic and can cause DNA damage and cancer.<sup>4</sup> Consequently, stringent regulations dictate a maximum allowable limit for chromium in industrial wastewater (for example a maximum of 5 ppm for total Cr, set by European Union Risk Assessment Report<sup>5</sup>) to safeguard the environment before any discharge takes place.

Adsorption is a well-developed method for treatment of groundwater and industrial wastewaters in general and for chromium removal in particular.<sup>2,3,6</sup> Several natural and synthetic carbon-



based materials are used for Cr adsorption studies<sup>3,6,7</sup>, some of which include activated carbon<sup>8</sup>, graphene, carbon aerogels and hydrogels and magnetic polymers.<sup>9,10</sup> Activated carbon, with its high surface area, abundance of surface functional groups, low cost, and potential for regeneration, is one of the most widely used materials in industrial adsorption processes for a wide range of contaminants.<sup>11</sup> Granular activated carbon (GAC), with particle sizes > 100  $\mu\text{m}$ , is ideal for fixed adsorption beds due to easy handling and minimal fine particle bleeding, while powdered activated carbon (PAC,  $d < 100 \mu\text{m}$ ) offers faster kinetics and higher surface area, making it ideal for batch adsorption and flow beds.<sup>12–14</sup>

Understanding the adsorption mechanisms of Cr(VI) and the key parameters that influence adsorption behavior is essential for developing materials with enhanced adsorption capacities and designing efficient adsorption processes. In Cr(VI) adsorption, factors such as functional groups, solution pH and ionic strength are particularly significant, as they strongly impact the adsorption capacity of carbon-based materials.<sup>8,11,15,16</sup> For example, in an acidic media, the surface functional groups of GAC are protonated,<sup>17,18</sup> acquiring either a positive or neutral charge (e.g., -OH, -COOH, -NH<sub>3</sub><sup>+</sup>), which attracts the dominant anionic Cr(VI) species through electrostatic interactions or hydrogen bonding. An ion exchange mechanism has been proposed where protonated functional groups such as C-OH<sub>2</sub><sup>+</sup> (protonated hydroxyl groups) interact with Cr(VI) ions.<sup>18</sup> Additionally, reduction reactions can occur on the GAC surface, converting Cr(VI) to Cr(III), due to electron transfer facilitated by surface functional groups.<sup>16,19</sup> Hydrogen bonding between oxygen or nitrogen functional groups and Cr(VI) species have also been proposed as one of the removal mechanisms on modified activated carbon surfaces.<sup>20–23</sup>

The adsorption capacity, as well as the conversion of Cr(VI) to Cr(III) of activated carbon can be improved through chemical modifications that add functional groups, enhancing interactions with Cr(VI). Alkaline treatments introduce oxygen functional groups including hydroxyl and carboxyl groups, promoting ion exchange and electrostatic attraction.<sup>24,25</sup> Nitric acid treatment for GAC has been found to enhance Cr(VI) removal efficiency by up to 70%, and increase the adsorption capacity by 2.5 times through the introduction of additional oxygen functional groups on the surface.<sup>26,27</sup> The Langmuir model was reported to represent the adsorption isotherm data best, suggesting a monolayer adsorption process. Incorporating heteroatoms such as nitrogen



and sulfur has also proven effective, as these atoms contribute additional adsorption or reactive sites, such as amine and sulfide groups, which aid Cr(VI) capture and conversion.<sup>8,15,16,19</sup> Abushawish et al. showed that a 45% improvement in Cr adsorption capacity can be achieved with nitrogen-doped GAC, prepared by an impregnation method in an ethanol medium. The Sips and Redlich-Peterson models were found to fit the adsorption isotherm of the modified GAC, suggesting a monolayer adsorption on a heterogeneous surface.<sup>8</sup> Regeneration efficiency is a critical parameter in the development of new adsorbents, as the economic feasibility of the process depends on the reusability of the adsorbent material. Various desorbing solutions have been employed to remove Cr species from saturated adsorbents and restore adsorption capacity. For carbon-based materials, regeneration is commonly achieved using NaOH, KOH, HCl, or HNO<sub>3</sub> solutions, typically in concentrations ranging from 0.1 to 1 M.<sup>3</sup>

While extensive research has explored the incorporation of nitrogen and sulfur heteroatoms into PAC, primarily during the synthesis stage using a carbon source and thiourea, studies on post-treatment modification of commercially available activated carbon remain scarce. Dual heteroatom doping (N/S) has been shown to improve Cr(VI) adsorption in various systems,<sup>16,28–30</sup> but its application to GAC, particularly through post-synthetic modification, has not been systematically examined. This study investigates whether such post-treatment doping is effective for enhancing Cr(VI) adsorption on GAC under a range of environmental conditions. In addition to adsorption capacity, isotherms, and kinetics, we also explore the impact of ionic strength up to 0.5 M NaCl. Furthermore, desorbed species during the regeneration process are analyzed and discussed as complementary evidence to XPS results, offering new insights into the underlying adsorption mechanisms. To the best of our knowledge, this is the first comprehensive study to address these aspects in N,S functionalization of GAC systems for Cr(VI) removal.

## 2. Materials and Methods

### 2.1. Materials



1 Acid-washed GAC (Coconut shell, mesh size 8 x 30, Newterra Co.), denoted as GAC, was used as  
2 the starting material. Thiourea (Fisher Scientific) was used as the source of nitrogen and sulfur in  
3 preparation of N/S functionalized GAC (denoted as N/S-GAC). Potassium dichromate  
4 (Anachemia) was used to prepare Cr(VI) solutions. Sodium chloride (Sigma Aldrich) was used to  
5 adjust the ionic strength of all solutions to values as indicated throughout this work. Hydrochloric  
6 acid (Sigma Aldrich), sodium hydroxide (Sigma Aldrich) and potassium hydroxide (Fisher  
7 Scientific) were used to adjust the pH of solutions and to prepare regeneration solutions.

## 8 2.2. Preparation of N/S functionalized GAC

9 N/S-GAC was prepared via a hydrothermal process in which 5 g of GAC was added to 100 ml of  
10 100 g/L thiourea solution and in a Teflon container. The container was then put in a steel  
11 autoclave and placed in a convection oven at 180 °C for 24 h to decompose the thiourea and  
12 functionalize the GAC surface with N- and S- containing groups. Then, after cooling at room  
13 temperature, the modified GAC was washed thoroughly with DI water to remove any excess  
14 materials (like unreacted thiourea or its products during decomposition in hydrothermal  
15 process), and dried at 100 °C overnight.<sup>28</sup>

## 16 2.3. Characterization

17 Nitrogen adsorption analysis (Micromeritics TriStar II) was conducted to evaluate the pore-size  
18 distribution (the distribution of pore diameters calculated from nitrogen adsorption–desorption  
19 isotherms), pore volume and surface area of the sorbents. The Barrett–Joyner–Halenda (BJH)  
20 method<sup>31</sup> was applied to calculate pore-size distribution (suitable for pores ~1–50 nm), while the  
21 Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area. SEM  
22 imaging (Quanta FEG 250 Field Emission SEM) was performed to obtain morphological  
23 information. FTIR analysis was conducted using KBr pellet method with Nicolet 4700 at 32 scans  
24 and a resolution of 4 cm<sup>-1</sup> for 500–4000 cm<sup>-1</sup>. Samples were crushed into fine powders and mixed  
25 with KBr powder in a 9:1 volumetric ratio (KBr:GAC) and pressed into pellets with 6 Ton press  
26 load. Raman Spectroscopy was performed on by a confocal Raman microscope (WITec Alpha-  
27 300) equipped with a diode laser operating at a wavelength of 532 nm and laser power of 5mW.  
28 CHNS elemental analysis was performed with ELEMENTAR UNICUBE analyzer. X-ray



photoelectron spectroscopy (XPS, Thermo-Fisher ESCALAB QXi) was performed using a monochromatic Al K $\alpha$  (1486.6 eV) radiation source and passing energy of 150 eV for survey scans (step size of 1 eV) and 30 eV for high-resolution scans (step size of 0.1 eV). Adsorbents were placed on the sample holder in granular form. XPS data analysis was done using CasaXPS software. All the spectra were calibrated with C-C binding energy of 284.8 eV as the reference. Peak fittings were done with constraining the FWHM and lineshape (Gaussian-Lorentzian and Lorentzian-Asymmetric models), and with Shirley model as background. Core-level peaks were added to each high-resolution spectrum by thorough study of literature.

Surface charge of the materials (point of zero charge) as a function of pH was measured with a Malvern Zetasizer Nano-ZS using the dynamic light scattering (DLS) method. Prior to this measurement, samples were first crushed into fine powder and then were suspended in solutions with different pH values using an ultrasound bath. UV-Vis absorption spectroscopy (Shimadzu UV-2600) at a wavelength of 350 nm was used to assess Cr(VI) concentrations and inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7000 Series) was carried out to measure total Cr concentrations in the solutions. For both UV-Vis and ICP-OES analyses, samples were diluted with 2% nitric acid to ensure Cr(VI) concentrations were below 50 ppm. The concentration of Cr(III) was then calculated by subtracting the Cr(VI) concentration from the total Cr concentration, assuming that no other chromium species were present.

#### 2.4. Adsorption and Regeneration Experiments

To measure the equilibrium and time-dependent adsorption capacity of our materials, batch adsorption experiments with a magnetic stirrer (450 rpm) were performed. Samples of solutions were taken and analyzed for chromium concentration by ICP-OES. The equilibrium adsorption capacity ( $q_e$ ) of the adsorbents was calculated using Eq. 1:

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad (\text{Eq.1})$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium Cr concentration,  $V$  is the volume of the solution and  $m$  is the mass of the adsorbent.





1 Isotherm studies were conducted for  $C_i = 20 - 250$  mg/L at pH = 5, in a 0.01 M NaCl solution at  
2 ambient temperature for an adsorption duration of 20 h. Kinetic experiments were carried out  
3 at  $C_i = 50$  ppm, in a 0.01 M NaCl solution at pH = 5, with an adsorbent dosage of 2 g/L for a  
4 duration of 20 h. The effects of pH (from 3 to 8) and ionic strength (0 to 0.5 M NaCl) were studied.  
5 Regeneration of adsorbents was performed using three desorption solutions, namely 1 M HCl,  
6 0.1 M NaOH and 0.1 M KOH, for 16 h (two-step regeneration, each step 8h). The regeneration  
7 (desorption) efficiency for each cycle was calculated as the ratio of the total amount of Cr species  
8 desorbed during regeneration to the total amount adsorbed.

### 10 3. Results and Discussions

#### 11 3.1. Incorporation of N-, S- groups in GAC

12 We incorporated N- and S- groups into GAC via the hydrothermal method described above. The  
13 physicochemical properties of GAC and N/S-GAC, including morphology, pore size distribution,  
14 surface area, and pore volume, play an important role in determining its effectiveness in the  
15 adsorption of Cr. The SEM micrographs of GAC and N/S-GAC (Figure 1a and 1b) show the  
16 presence of large pores (a few microns) on the surface, however, no major difference can be  
17 observed between the two adsorbents. The  $N_2$  adsorption analyses show that N/S-GAC has lower  
18 surface area (by 15%) and pore volume (by 17%) than GAC (Table 1). Moreover, pore-size  
19 distribution plots in Figure 1c suggests the presence of micropores for both adsorbents and that  
20 the proposed modification does not change the adsorbents significantly. This can be attributed  
21 to pore blockage by the products of thiourea decomposition, such as carbodiimide ( $HN=C=NH$ ).<sup>32</sup>  
22 XPS elemental analysis of the GAC and N/S-GAC, presented in Table 1, confirms the presence of  
23 nitrogen (1.64 at.%), sulfur (1.04 at.%), and oxygen (4.69 at.%) on N/S-GAC surface. In contrast,  
24 the GAC surface contained negligible sulfur (0.06 at.%) and nitrogen (0.27 at.%), with an oxygen  
25 content of 6.29 at.%. CHNS analysis (Table 1) was conducted to compare the bulk composition  
26 with surface composition from XPS. Surprisingly, bulk nitrogen content was significantly smaller  
27 than that of the surface (0.72 at.% vs. 1.64 at.%), while bulk sulfur was slightly larger than surface  
28 (1.23 at.% vs. 1.04 at.%). This implies that nitrogen species penetrated the pore structure less





effectively than sulfur. To gain deeper insight into the nature of sulfur-, nitrogen-, and oxygen-containing functional groups on the GAC surface, high-resolution XPS analysis was conducted on both GAC and N/S-GAC (Figure 2b-g). The XPS survey spectra of GAC and N/S-GAC, presented in the Supplementary Information (Figure S2), show the presence of O, N, and S atoms in addition to carbon. The C1s spectra (Figure 2b and 2c) confirms the presence of hydroxyl (286.3 eV), carbonyl (287.8 eV), and carboxylic (288.8 eV) groups.<sup>33,34</sup> Deconvolution of the N1s spectrum indicates that the majority of the nitrogen (69.5%) is present as amine groups, with a binding energy centered at 399.7 eV. Protonated amine groups made up the rest of the incorporated nitrogen at 402.5 eV (30.5%). The S2p spectra shows the doublet peaks at 164.3 eV and 165.5 eV, attributed to C-S-C bonding environment (S2p<sub>3/2</sub> and S2p<sub>1/2</sub>), as well as the doublet at 168.4 eV and 169.6 eV attributable to sulfonic groups (-SO<sub>x</sub>, 35%).

Table 1. Structural properties and elemental composition of adsorbents.

	N <sub>2</sub> Adsorption		Elemental analysis (at. %) - CHNS				Elemental analysis (at. %) - XPS			
	S <sub>total</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	C	N	S	O	C	N	S	O
GAC	987.93	0.42	94.81	0.23	0	4.73	93.38	0.27	0.06	6.29
N/S-GAC	835.54	0.35	95.52	0.72	1.23	2.53	92.63	1.64	1.04	4.69



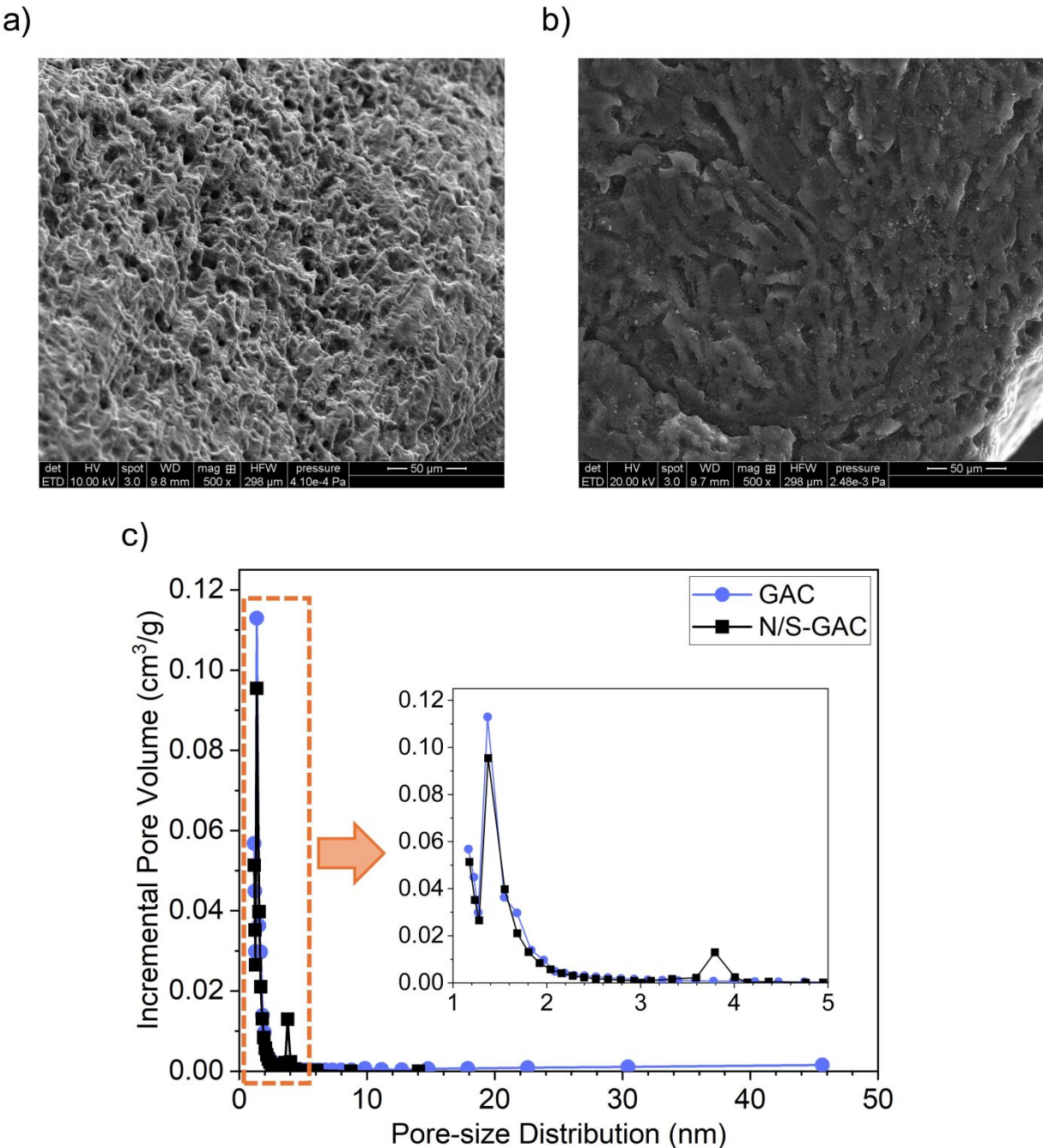


Figure 1. SEM micrographs of a) GAC and b) N/S-GAC. Large pores (micron-sized) can be seen on both materials, suggesting the presence of macropores which could not be detected with N<sub>2</sub> adsorption analysis; c) Pore-size distribution of GAC and N/S-GAC obtained using fitting of N<sub>2</sub> adsorption data by BJH model. The figure shows that for both materials, micropores (pore-size less than 2 nm) are dominant and almost no mesopores (pore-size between 2 and 50 nm) are seen.

1 We also employed FTIR and Raman Spectroscopy to identify different heteroatoms and their  
2 groups and structural disorders in GAC and N/S-GAC (Figure 2a and Figure S1). For the unmodified  
3 GAC, three major FTIR peaks can be seen:  $\sim 1060\text{--}1160\text{ cm}^{-1}$  attributed to C-O stretching,<sup>35</sup>  $\sim 1575$   
4  $\text{cm}^{-1}$  attributed to C=C stretching, and  $\sim 3440\text{ cm}^{-1}$  related to O-H stretching (hydroxyl groups).<sup>36</sup>  
5 After incorporating N and S, a more pronounced peak at  $3400\text{--}3500\text{ cm}^{-1}$  is associated with N-H  
6 stretching (amine group). At  $1060\text{--}1160\text{ cm}^{-1}$ , S=O stretching (sulfonic group) and C-N stretching  
7 (amine group) are responsible for the peak broadening and increased intensity.<sup>35</sup> Raman spectra  
8 of GAC and N/S-GAC is shown in Figure S1. The two main Raman peaks of carbon-based materials,  
9 the D-band at  $\sim 1340\text{ cm}^{-1}$  and the G-band at  $\sim 1600\text{ cm}^{-1}$  are present as expected. D-band  
10 represents the degree of disorder in  $\text{sp}^2$ -hybridized carbon caused by edge sites, functional  
11 groups and pores, while G-band represents in-plane stretching vibrations of  $\text{sp}^2$ -hybridized  
12 graphitic structure. The  $I_D/I_G$  ratio for GAC and N/S-GAC was  $1.15 \pm 0.02$  and  $1.19 \pm 0.03$ ,  
13 respectively. The slight increase in the  $I_D/I_G$  ratio in the N/S-GAC is likely due to the defects added  
14 through functionalization with N and S.



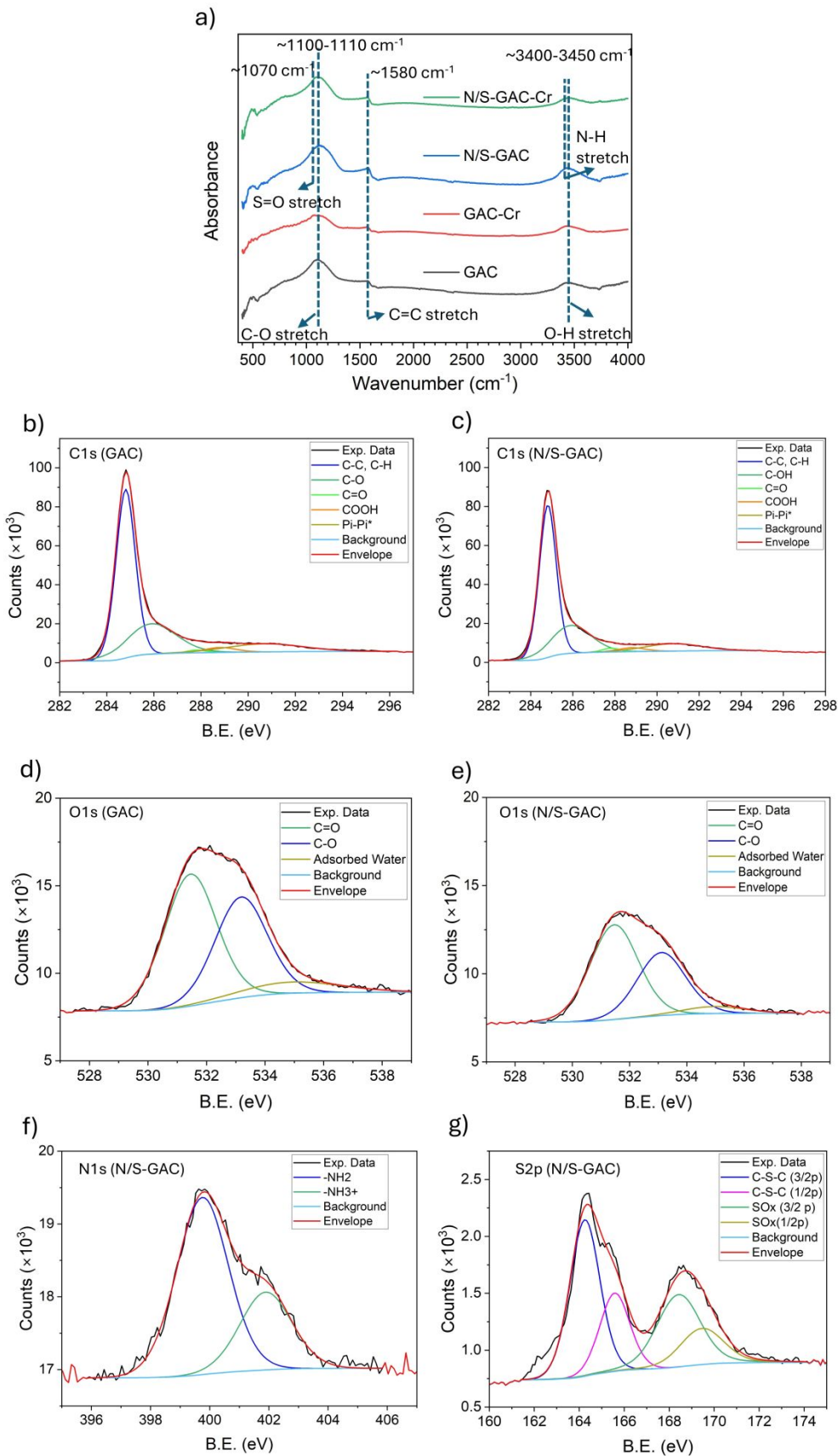


Figure 2. a) FTIR spectra of GAC and N/S-GAC, before and after adsorption. Enhancement in peaks 1060-1160  $\text{cm}^{-1}$  and 3300-3500  $\text{cm}^{-1}$  for N/S-GAC, compared with GAC is attributed to presence of S=O and C-N and N-H bonding, respectively. b-g) High-resolution XPS spectra of b,c) C1s for GAC and N/S-GAC, d,e) O1s for GAC and N/S-GAC, and f,g) N1s and S2p for N/S-GAC.

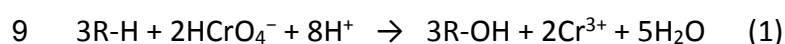
## 3.2. Performance

### 3.2.1. The Effect of pH and Ionic Strength

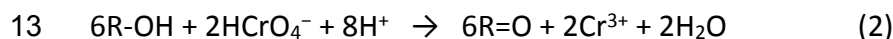
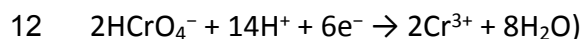
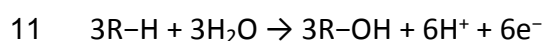
The pH of a solution determines the Cr speciation, charge state of the adsorbents' surface species, which both can impact the adsorption process and performance. We investigated the effect of the initial pH of the solution on Cr(VI) removal for unmodified and modified GAC adsorbents over a range from pH 3 to 8, using an initial Cr(VI) concentration of 50 ppm and a 0.01 M NaCl background solution. The results, shown in Figure 3a, suggest that lower initial pH (below 4) is favorable for removal of Cr(VI) for both GAC and N/S-GAC. The adsorption capacity significantly decreased as the pH increased 3 to 8 (from 20.0 to 1.0 mg/g for GAC and 23.3 mg/g to 4.6 mg/g for N/S-GAC). Similar trends were observed in previous studies of carbon based adsorbents, where low initial pH in the range 2-4 resulted in higher adsorption capacity, with a significant (3- to 5-fold) decrease in capacity as the pH increased.<sup>8,15,19,21</sup> Possible reasons for higher capacity at lower pH generally include: (1) positive surface charge (positive zeta potential) which can result in electrostatic attraction; (2) specific interactions between functional groups and Cr (VI) species (such as hydrogen bonding or ion exchange); and (3) reduction of Cr(VI) due to the abundance of  $\text{H}^+$ . Zeta potential measurements (Figure S3) show that point of zero charge for unmodified GAC and N/S-GAC was around pH 2.0 and 3.0, respectively. Above this pH the surface is negatively charged and tends to repel anions, including all Cr(VI) ions (Figure S4). The acid dissociation constant ( $\text{pK}_a$ ) for protonation of oxygen functional groups such as hydroxyl groups ( $-\text{OH}_2^+/-\text{OH}$ ) is typically very low ( $\text{pK}_a < 0$ )<sup>37</sup>, hence, electrostatic attraction is not a dominant mechanism in this system. Hydrogen bonding between -OH in  $\text{HCrO}_4^-$  and oxygen functional groups such as -COOH and -OH is the most probable interaction mechanism, since hydrogen bonding energy can be larger than that of the electrostatic repulsion (see calculations in the Supplementary Information, Section S1). As the pH increases,  $\text{CrO}_4^{2-}$  becomes the dominant



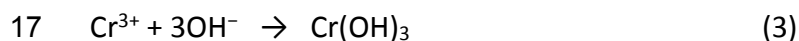
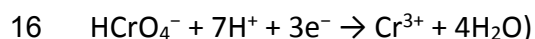
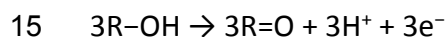
Cr(VI) species, and the capacity decreases due to weaker hydrogen bonding between -OH and -O<sub>2</sub>Cr, the abundance of OH<sup>-</sup> as competing anions, and larger electrostatic repulsion as the surface charge and the anion charge both increase. At acidic pH, adsorption through reduction reaction pathways may also occur, since the H<sup>+</sup> and surface functional groups that act as electron donors are more abundant. This will lead to formation of Cr (III) species<sup>16,38</sup>, which are positively charged at pH < 6 (provided electrostatic attraction to the adsorbent surface), and precipitate as Cr(OH)<sub>3</sub> at higher pH values.<sup>39</sup> Reactions 1, 2 and 3 summarize the mechanism of reduction and Cr(OH)<sub>3</sub> formation.



(Redox Reactions:



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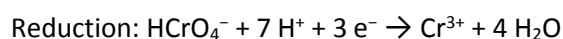
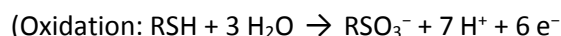
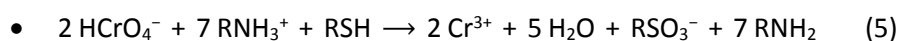
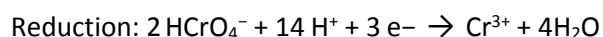
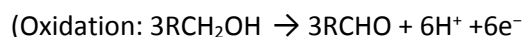
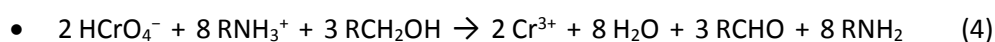


The adsorption results indicate that N and S functionalization improves the capacity of the GAC at all pH studied, with the highest capacity of 23 mg/g obtained at pH 3. N- functional groups can be protonated at low pH<sup>16</sup> (e.g. amine groups with pK<sub>a</sub>(-NH<sub>3</sub><sup>+</sup>/-NH<sub>2</sub>) ≈ 9<sup>37,40</sup>), leading to a more positive surface charge compared to the unmodified GAC, and thus enhanced electrostatic attraction of Cr(VI) anions, resulting in a higher adsorption capacity.<sup>17</sup> N and S functional groups also take part in hydrogen bonding with Cr (VI) species, which is not readily affected by pH change<sup>21,22</sup>. N and S functional groups can also act as electron donors for the reduction of Cr(VI) to Cr(III)<sup>16,19,38</sup> in the presence of H<sup>+</sup>, further increasing the adsorption capacity.

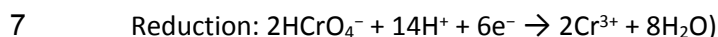
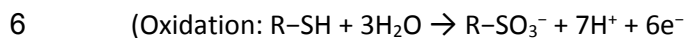
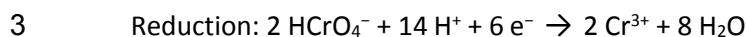
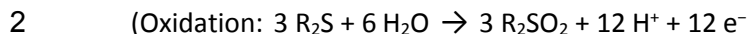
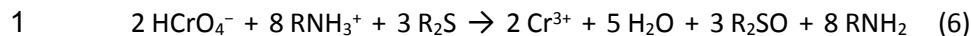




The Cr2p XPS spectra of adsorbents after Cr adsorption are shown in Figure 2c and 2d. The presence of Cr(III) was confirmed for both GAC and N/S-GAC, accounting for 66.6% and 83.2% of the total Cr, respectively. Previous studies have reported similar XPS spectra for Cr adsorbed on carbon materials, indicating reduction reaction as one of the main adsorption mechanisms.<sup>19,41</sup> FTIR analysis (Figure 2a) shows several peaks relating to oxygen, nitrogen and sulfur groups were reduced in size (peaks at 1060-1160 cm<sup>-1</sup> and 3300-3500 cm<sup>-1</sup> exhibit lower intensities) for the adsorbents after Cr adsorption, suggesting that functional groups play an important role in the adsorption process<sup>8,42,43</sup>. The N1s and S2p spectra of N/S-GAC after adsorption are presented in Figures 3e and 3f, respectively. A notable decrease in the proportion of protonated amine groups (–NH<sub>3</sub><sup>+</sup>) was observed after Cr Adsorption. Protonated amine groups accounted for 14.6% of the total nitrogen after Cr adsorption on N/S-GAC, compared to 30.5% prior to adsorption, indicating their involvement in the adsorption process. Protonated amine groups can act as proton reservoirs, providing H<sup>+</sup> for the reduction reaction, while oxygen and sulfur functional groups such as –OH, –SH and C–S–C act as electron donors. The content of oxidized sulfur species (–SO<sub>x</sub>) increased from 35.0% to 60.6% after Cr adsorption, suggesting the formation of additional sulfur–oxygen functionalities. Figure 3f shows that some S–H/C–S–C groups remain unutilized after adsorption. This may be attributed to diffusion limitations, either by blockage of underneath S group by Cr(III) hydroxide formed by reduction reactions, or restricted accessibility due to microporous structure of the N/S-GAC (Figure 1c) for HCrO<sub>4</sub><sup>–</sup> anions. Possible reduction reactions that may occur in the system based on these observations include:







The O 1s spectra in Figure S6 for both GAC and N/S-GAC show an increase in the C=O and Cr–OH components around ~531.7 eV, indicating the formation of these species during adsorption. The –NH<sub>2</sub> peak was observed to shift slightly, from 399.7 to 400.3 eV, during the Cr adsorption on N/S-GAC. This may be due to hydrogen bonding between N–H and HCrO<sub>4</sub><sup>–</sup>, which withdraws electron density from the nitrogen group and increases the binding energy. Section S2 of the Supplementary Information provides additional details on the influence of nitrogen functional groups and solution pH on the reduction mechanism.

Wastewater effluents usually contain dissolved ions such as chloride (200–4000 ppm) and sulfate (150–1000 ppm) in addition to the heavy metals.<sup>44,45</sup> The presence of co-ions in the solution typically reduces the adsorption capacity of the adsorbent. For Cr(VI), since it exists in anionic form, other anions may influence the adsorption capacity due to competition for active sites. In this study, the effect of NaCl concentration on Cr(VI) adsorption was investigated at pH 5 and an initial Cr(VI) concentration of 50 ppm, as shown in Figure 3b. As expected, the highest Cr adsorption capacity (17.9 mg/g for N/S-GAC and 13.7 mg/g for GAC) was observed when no NaCl was present. As the salt concentration was increased, the Cr adsorption capacity decreased, reaching 8.5 and 5.3 mg/g at 0.5 M NaCl for N/S-GAC and GAC respectively. The rate of decrease in Cr(VI) adsorption capacity at NaCl concentrations higher than 0.1 M (5.8 g/L ≤) drops significantly. Similar trends have previously been reported,<sup>46,47</sup> with the adsorption capacity of activated carbon reaching a plateau at NaCl concentrations greater than 0.3 M NaCl.



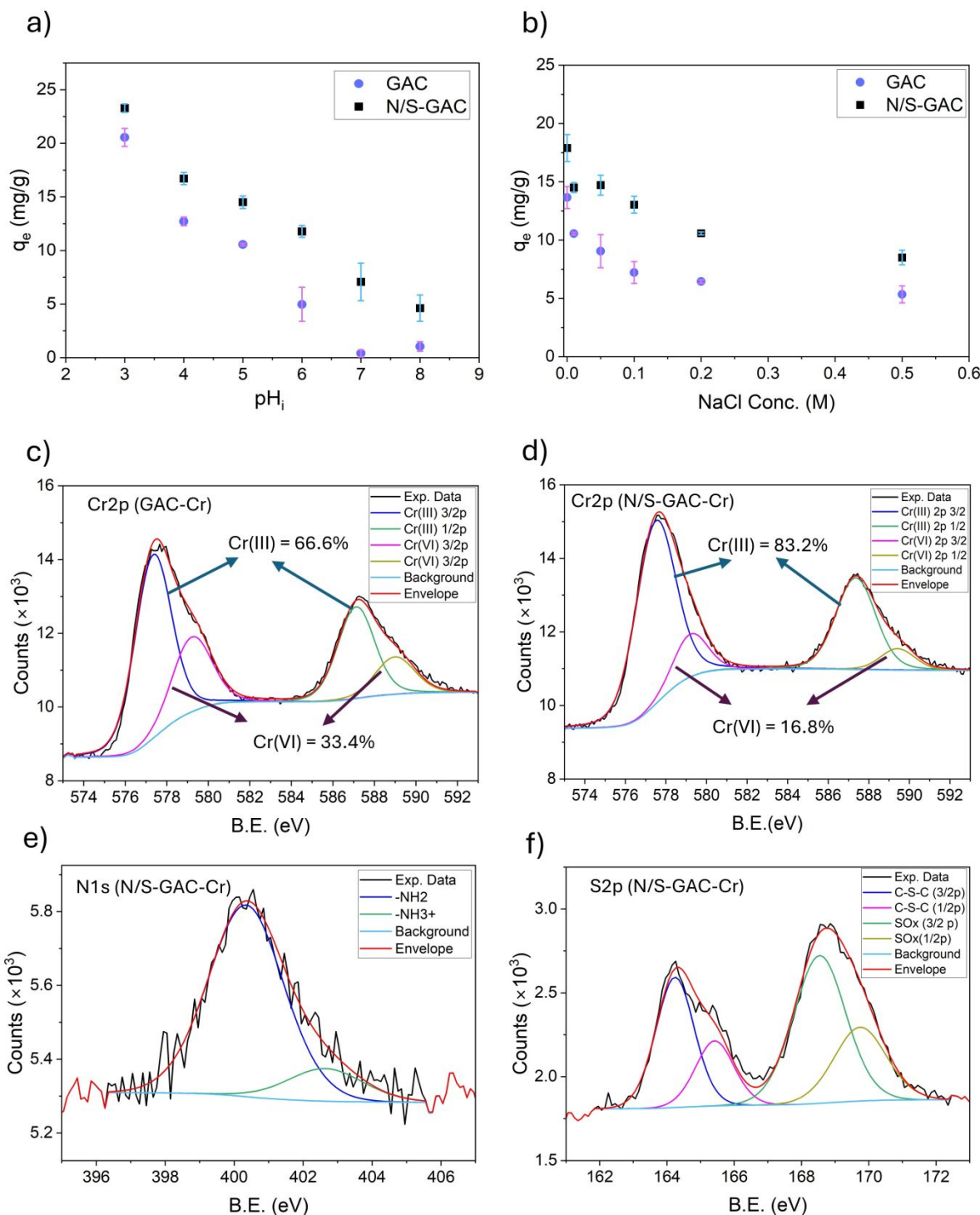


Figure 3. a) Cr loading as a function of pH (Conditions:  $C_i$  = 50 ppm,  $t$  = 20 h, adsorbent dosage = 2 g/L, ionic strength = 0.01 M NaCl); b) Cr loading as function of ionic concentration (Conditions: pH = 5,  $C_i$  = 50 ppm,  $t$  = 20 h, adsorbent dosage = 2 g/L); Cr 2p spectra of c) GAC and d) N/S-GAC after adsorption and e) N 1s and f) S 2p spectra of N/S-GAC-Cr.



N1s and f) S2p spectra of N/S-GAC after adsorption ( $\text{pH}_i = 5$ ,  $C_i = 50$  ppm,  $t = 20$  h, adsorbent dosage = 2 g/L).

### 3.1.2. Regeneration

The regeneration of adsorbents serves as one of the benchmarks for designing a practical adsorption system. Often, adsorption capacity declines with each cycle, resulting in progressively worse performance. Both alkaline and acid solutions were evaluated for adsorbent regeneration, including 0.1 M NaOH, 0.1 M KOH, and 1 M HCl solutions. Figure 4a shows the result of desorption of chromium from GAC and N/S-GAC for the first cycle. On GAC, the 0.1 M NaOH and 0.1 M KOH solutions performed similarly with Cr desorption efficiencies of > 90%. This can be explained by electrostatic repulsion as follows: at high pH, surface functional groups (OH, COOH,  $\text{NH}_3^+$ ) become deprotonated, making the surface highly negative. This results in increased electrostatic repulsion between chromate anions and negatively charged surface which in turn either eliminates or reduces the extent of attractive hydrogen bond network. On the other hand, 1 M HCl solution showed significantly lower regeneration performance (< 40% desorption for 1st cycle). This is most likely due to the stability of hydrogen bonds at low pH. In the case of NaOH and KOH, both Cr(VI) and Cr(III) were desorbed. However, when a 1 M HCl solution was used, most of the desorbed Cr species was in the form of Cr(III). For GAC, the total amount of Cr(III) in the regeneration solution was substantially higher when using an HCl solution than that obtained with alkaline solutions (33% vs. 3.5% of total Cr adsorbed). The increased presence of Cr(III) with the HCl regenerant can be attributed to a reduction reaction occurring during desorption, as the abundance of  $\text{H}^+$  ions create a favorable environment for Cr(VI) reduction (Providing  $\text{H}^+$  for Reactions 1 and 2).



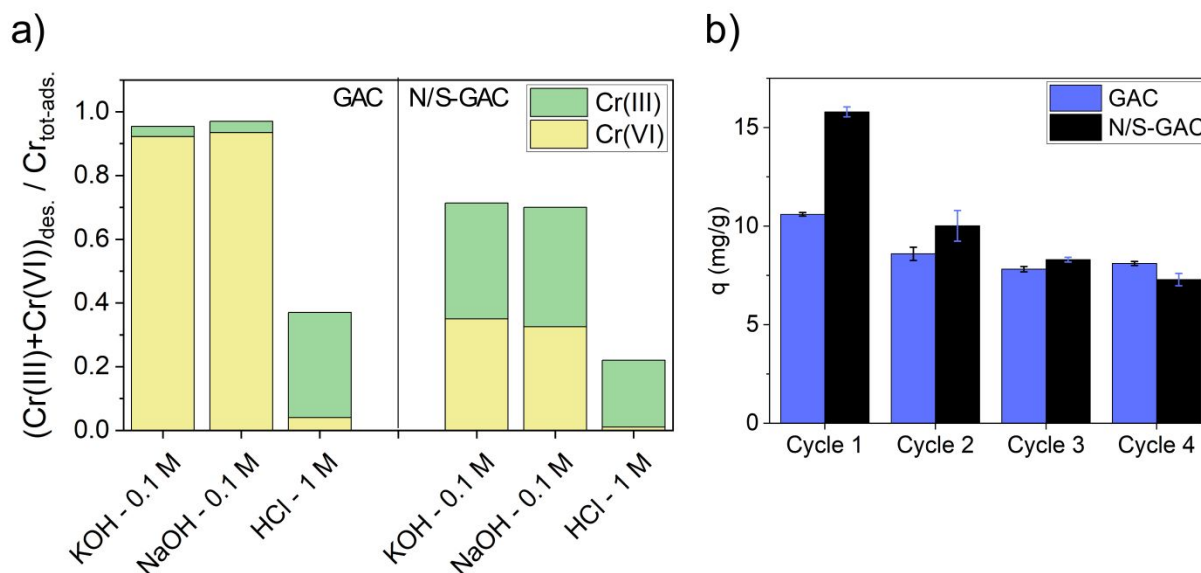


Figure 4. a) Desorption efficiencies and amount of Cr species desorbed for regeneration solutions 0.1 M KOH, 0.1 M NaOH and 1M HCl, Conditions: Two-step desorption, each step  $V_{\text{sol}} = 50$  ml and  $t = 8$  h, b) Cyclic regeneration performance of GAC and N/S-GAC with KOH 0.1 M as the regeneration solution, Conditions: Two-step desorption, each step  $V_{\text{sol}} = 50$  ml and  $t = 8$  h.

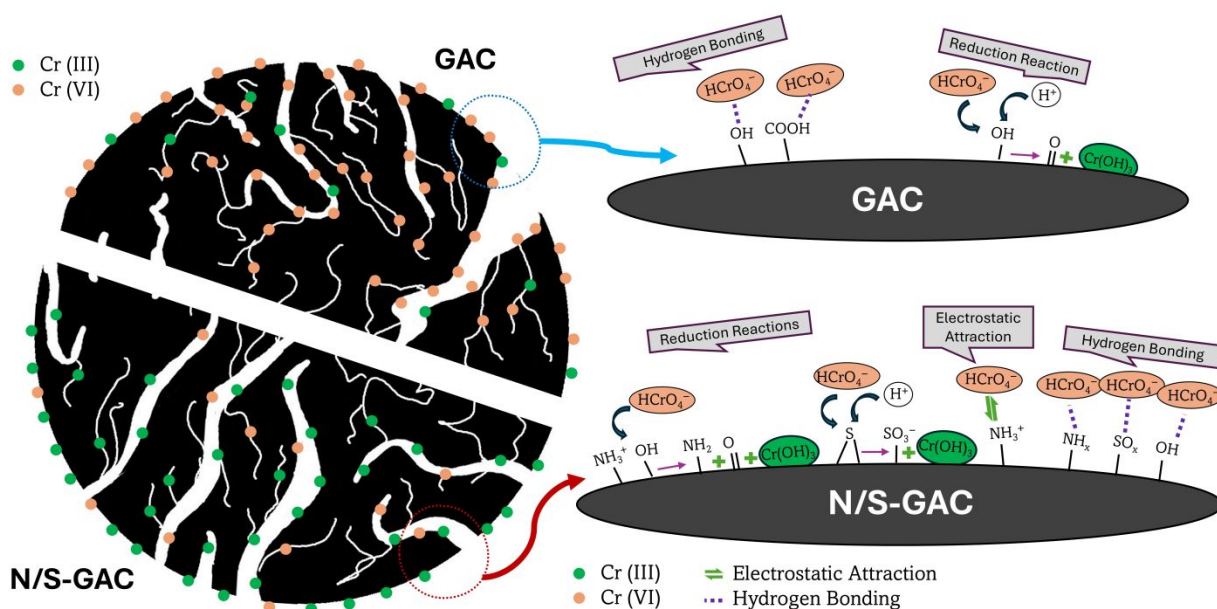
Table S1 provides more detailed analysis of desorbed species by ICP-OES and UV-Vis, and comparison with XPS data. For GAC, UV-Vis analysis shows that ~9.3 mg/g of Cr is desorbed as Cr(VI) during regeneration, corresponding to ~90% of the total adsorbed Cr. The remaining fraction is mainly desorbed as Cr(III) in the HCl step, accounting for ~10% of the total. However, speciation results for Cr on GAC (Figure 3c and Figure S6) indicate that Cr(III) species dominate (~67% after adsorption and ~81% after regeneration), which contradicts the ICP-OES and UV-Vis results for the desorbed species. This discrepancy can be attributed to the preferential formation of Cr(III) hydroxides on the external surface of GAC granules. Since XPS is highly surface-sensitive, probing only the top few atomic layers, it detects these surface species more readily than those confined within the micro- and mesopores of GAC.

For N/S-GAC, ~3.8 mg/g of Cr(VI) was desorbed during regeneration based on analysis of desorbed species, corresponding to 23% of the total adsorbed Cr. In addition, ~7.6 mg/g of Cr was desorbed as Cr(III), accounting for 45% of the total. The remaining 32% of Cr on N/S-GAC was



1 identified by XPS analysis in Figure S6, which indicated that the majority was present as Cr(III)  
2 (85% of Cr remained after regeneration). These species do not dissolve during regeneration and  
3 remain irreversibly bound to the surface. Comparison of desorption data from ICP-OES and UV-  
4 Vis analyses with XPS results after adsorption (Figure 3d) shows a slight discrepancy with the Cr  
5 species, which again arises from the surface sensitivity of XPS and its strong response to Cr(III)  
6 species concentrated on the outer surface. Overall, these findings suggest that for GAC, hydrogen  
7 bonding of  $\text{HCrO}_4^-$  anions could be considered as the dominant mechanism with minimal  
8 reduction happening on outer surface, whereas for N/S-GAC, reduction is the main mechanism  
9 of Cr(VI) removal during the first adsorption cycle, with Cr(III) hydroxides heterogeneously  
10 distributed on the outer surface and bulk of the adsorbent. Some reduced species remaining  
11 irreversibly bound and others extractable by KOH and HCl regeneration. This is attributed to the  
12 functional groups on N/S-GAC, that promote the reduction of Cr(VI) during the adsorption  
13 process.<sup>16,19,41</sup> This difference is also reflected in isotherm analysis in Section 3.1.3. It should be  
14 noted that the formation of surface Cr(III) hydroxides may lead to biased XPS results, and thus  
15 complementary techniques such as ICP-OES and UV-Vis provide more reliable information by  
16 accounting for both surface and bulk contributions. Scheme 1 summarizes the adsorption  
17 mechanisms for the GAC and N/S-GAC discussed above. A summary of XPS analyses for GAC and  
18 N/S-GAC has been provided in Figure S8 and Figure S9, respectively.





Scheme 1. Schematic of the adsorption process on GAC and N/S-GAC. For GAC, Cr(VI) is primarily bound to the surface through hydrogen bonding, with only a small fraction reduced to Cr(III). In contrast, for N/S-GAC, reduction is the dominant pathway during the first adsorption cycle, while from the second cycle onwards, hydrogen bonding and electrostatic attraction become the main mechanisms.

The regeneration performance of GAC and N/S-GAC was investigated over multiple adsorption-desorption cycles using 0.1 M KOH as the regeneration solution (Figure 4b). The regeneration efficiency for GAC had a gradual decrease with each cycle, with the initial capacity of 10.6 mg/g decreasing to 8.1 mg/g on the fourth cycle. For the GAC, as expected the Cr(VI) is predominant species in the regeneration solutions throughout the multiple cycle regeneration. For N/S-GAC, while new N and S functional groups showed significant improvement in the first cycle, their participation in adsorption reduced in the subsequent cycles, which led to a decrease in the regeneration efficiency, and the performance of N/S-GAC and GAC became similar after the second cycle. This decrease in performance may be attributed to a decrease in the reducing ability of N/S-GAC after the first cycle, as regeneration process does not reactivate these reduction sites (Figure S6 and Figure S10). This reduction in adsorption was reported for N-doped GAC previously, where 15% to 20% of the initial capacity is lost after the first cycle.<sup>8,15</sup>





Addressing irreversible oxidation is critical for practical deployment, as it directly influences cost-effectiveness, lifespan of the adsorbent, and process sustainability. Some strategies for preserving the N,S- functionality include (i) more robust regeneration strategies that can partially restore or protect the active sites, such as electro-regeneration where the oxidized sites can be reduced or (ii) periodic re-functionalization of the adsorbent, if possible.

### 3.1.3. Adsorption Isotherm and Kinetics

Isotherm and kinetic studies were carried out for Cr(VI) adsorption on both GAC and N/S-GAC to validate the adsorption mechanisms proposed in the preceding sections. As shown in Figure 2, the initial solution pH has a significant influence on Cr(VI) uptake by both adsorbents. In the absence of pH adjustment, solutions with initial Cr(VI) concentrations ranging from 10 to 100 mg/L exhibited pH values between 4.5 and 5. Accordingly, a pH of 5 was selected for the isotherm and kinetic experiments. As shown in Figure 5a, the adsorption capacity increased with initial Cr(VI) concentration without reaching a plateau, indicating unsaturated active sites across the tested range. N/S-GAC consistently outperformed GAC, which was attributed to the presence of N and S functional groups.

Isotherm data were fitted using non-linear regression to common models: Freundlich, Langmuir, Temkin, Sips and Redlich-Peterson (Table S2, Figure S11). Table S3 summarizes the model parameters obtained from each fitting, along with the 95% confidence intervals, correlation coefficients ( $R^2$ ), and sum of square root of errors (SSE). The Sips model best described the adsorption behavior of GAC, showing high  $R^2$ , low SSE, and narrow confidence intervals, suggesting a monolayer adsorption process on a surface that may be heterogeneous or homogeneous, with heterogeneity arising from the distribution of adsorption energies among surface active sites. This is consistent with the regeneration results, which indicate relatively uniform adsorption of Cr(VI) as  $\text{HCrO}_4^-$  on the GAC surface. In contrast, for N/S-GAC, although both the Sips and Redlich-Peterson models produced good fits (low SSE and high  $R^2$ ), the parameters exhibited very broad 95% confidence intervals (Table S3), indicating that the additional parameter does not provide meaningful interpretive value. This likely reflects strong





correlation among the model parameters.<sup>48</sup> The Freundlich model, in turn, offered a better balance of fit quality and parameter reliability, with higher  $R^2$ , lower SSE, and comparatively narrow confidence intervals, making it the most suitable model for describing adsorption on N/S-GAC. This finding is consistent with previous observations of heterogeneous Cr(III) hydroxide formation near N and S functional groups, as confirmed by ICP-OES and UV-Vis analyses.

The kinetics of Cr adsorption exhibit two regimes (Figure 5b), a rapid initial regime during the first 200 min, followed by a slower adsorption towards equilibrium. In the fast regime, adsorption rates on GAC and N/S-GAC are similar ( $\sim 0.108$  mg/(g.min) vs.  $0.113$  mg/(g.min), respectively). On the other hand, Cr adsorption is faster on N/S-GAC than GAC in the slow regime ( $\sim 0.001$  mg/(g.min) vs.  $0.003$  mg/(g.min), respectively), with the higher adsorption capacities on N/S-GAC becoming more apparent. Given that the enhanced adsorption capacity on N/S-GAC arises from its adsorption-reduction ability rather than differences in surface area or porosity, the faster adsorption rate at longer adsorption times in N/S-GAC is attributed to the adsorption-reduction process. Similar kinetic trends have been reported for activated carbon systems. The kinetic data were analyzed using pseudo-first order, pseudo-second order (PSO), revised pseudo-second order (r-PSO, removes the necessity of constant adsorbate concentration in PSO), Elovich, Boyd-Reichberg, and Weber-Morris models (described in Table S4). Among these, r-PSO provided the best fit for both GAC and N/S-GAC, based on  $R^2$  and SSE values, indicating chemisorption as the rate-limiting step (please refer to Table S5, Figure S12). The slow regime ( $200 \text{ min} < t$ ) has been fitted with the models separately and the rate constants have been included in Table S6 in the Supplementary Information. The Weber-Morris model (Figure S13) also shows that there are clearly two stages involved in the adsorption process; the first stage can be attributed to the film diffusion with larger constant rates, and the second stage with smaller constant rates assigned to pore-diffusion of adsorbate species. Prior studies on N and S-doped activated carbon have also identified PSO as the most appropriate model, supporting chemisorption as the dominant mechanism.<sup>16,19,21,28–30</sup> Notably, given the small pore sizes ( $< 2$  nm) of both GAC and N/S-GAC (Figure S1), intraparticle diffusion likely governs the initial adsorption stage. However, the assumption of constant adsorbate concentration during the adsorption process in conventional diffusion models (and also PSO model) may not fully apply under the experimental conditions.<sup>49</sup>



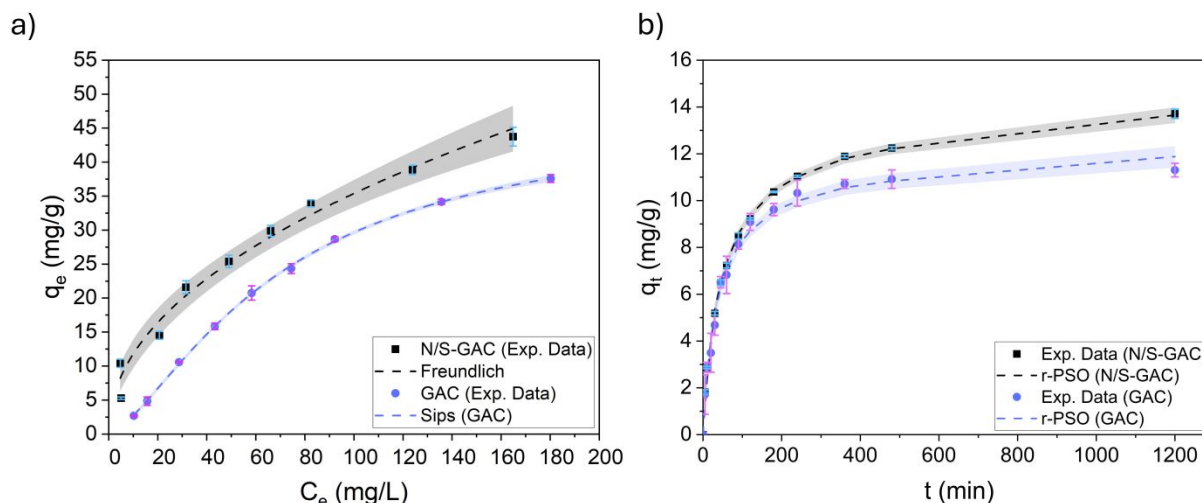


Figure 5. a) Adsorption data and best-fitted isotherms for GAC and N/S-GAC. (Condition:  $C_i = 25\text{--}250$  ppm, pH = 5, adsorbent dosage = 2 g/L,  $T = 22^\circ\text{C}$ ); b) Adsorption kinetics and best fitted model (Condition:  $C_i = 50$  ppm, pH = 5, adsorbent dosage = 2 g/L,  $T = 22^\circ\text{C}$ ). Shaded areas are representative of 95% confidence intervals for the fits.

## 4. Conclusions

In this study, we investigated the effect of simultaneous nitrogen and sulfur incorporation into commercial GAC using a simple one-pot hydrothermal post-treatment method for Cr(VI) adsorption. Characterization by FTIR and XPS confirmed the successful formation of functional groups such as amines, sulfides, and sulfonic group, which enhanced adsorption performance. Although the modification resulted in a 15% reduction in surface area which is usually unfavorable, the N/S-GAC showed improved Cr(VI) adsorption across a broad pH range (3–8) and in the presence of high ionic strength (up to 0.5 M NaCl), with the highest uptake at pH 3. Isotherm modeling suggested a shift in adsorption mechanism: the Sips model best described unmodified GAC, while the Freundlich model better fit the N/S-GAC data, indicating a transition from predominantly monolayer physisorption of  $\text{HCrO}_4^-$  to heterogeneous adsorption involving chemical reduction. Kinetic analysis using the revised pseudo-second-order model pointed to chemisorption as the rate-limiting step.



To gain further insight into the adsorption mechanism, we compared surface species identified by XPS with desorbed species analyzed by ICP-OES and UV-Vis after regeneration. XPS results showed the presence of Cr(III) on the adsorbents' surface, suggesting reduction of Cr(VI) for both GAC and N/S-GAC which happens along with hydrogen bonding of Cr(VI) species to O-H/N-H groups and electrostatic attraction of Cr(VI) species to protonated amine group ( $-\text{NH}_3^+$ ). The analysis of the desorption solutions revealed that Cr(VI) was the dominant species released from GAC, indicating that reduction was limited or did not occur extensively. This discrepancy underscores the limitations of relying solely on XPS for speciation and highlights the importance of complementary solution-phase analysis. Our approach, combining surface and desorbed species analysis, provides a more accurate understanding of the reduction behavior and adsorption mechanism, and to the best of our knowledge, has not previously been applied to N,S-functionalized activated carbon systems. Regeneration studies further showed that alkaline desorption (using NaOH or KOH) was more effective than acidic conditions, although some Cr remained irreversibly bound, leading to performance decline over successive cycles and apparent loss of reduction capability. This points to the need for improved regeneration strategies; ongoing work is exploring electrochemical regeneration to address this limitation.

Overall, our findings demonstrate that post-synthetic N,S-functionalization of GAC is a promising route to enhance Cr(VI) adsorption. Moreover, the integration of desorbed species analysis with surface characterization provides deeper insight into adsorption mechanisms and reveals that Cr(VI) reduction on activated carbon may be less extensive than previously assumed. These results contribute to the development of more effective adsorbents for water treatment and set a foundation for more robust mechanistic investigations.

## 5. Data Availability

The data supporting this article have been included in the main text and the Supplementary Information document.

## 6. Conflict of Interest



There are no conflicts to declare.

## 7. Acknowledgements

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## Data Availability Statement

The data supporting this article have been included in the main text and the Supplementary Information document.

