

Research Article

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A theoretical and experimental study of the adsorptive removal of hexavalent chromium ions using graphene oxide as an adsorbent

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Abstract: This study is focused on the adsorption of hexavalent chromium ions Cr(VI) using graphene oxide (GO). The GO was prepared by chemical oxidation (Hummers method) of graphite particles. The synthesized GO adsorbent was characterized by Fourier transform infrared spectroscopy and UV-Vis spectroscopy. It was used for the adsorption of Cr(VI) ions. The theoretical calculations based on density functional theory and Monte Carlo calculations were used to explore the preferable adsorption site, interaction type, and adsorption energy of GO toward the Cr(VI) ions. Moreover, the most stable adsorption sites were used to calculate and plot non-covalent interactions. The obtained results are important as they give molecular insights regarding the nature of the interaction between GO surface and the adsorbent Cr(VI) ions. The found adsorption energy of -143.80 kcal/mol is indicative of the high adsorptive tendency of this material.

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The adsorption capacity value of GO toward these ions is $q = 240.361$ mg/g.

Keywords: graphene oxide, hexavalent chromium, adsorption, DFT, Monte Carlo calculations

1 Introduction

As a result of human activity (mining, chemical industry, manufacturing, agriculture, etc.), water resources are partially contaminated to some extent, and this problem continues to be present. Heavy metals also contribute to this variety of chemical pollutants, as effluent products or by-products of the industry [1–3]. These pollutants are of great and long-lasting concern for environmental and health safety due to their properties such as nonbiodegradability and bioaccumulation ability in living organisms [1,4]. A common heavy metal polluting species found frequently in the environment is hexavalent chromium ions Cr(VI) [5]. Generally, chromium exists in several stable oxidation states such as Cr(0) , the trivalent Cr(III) , and the hexavalent Cr(VI) species. Cr(VI) ions in the forms of chromate, dichromate, and chromium trioxide are considered the most toxic forms of chromium. In this form, they possess an increased oxidizing potential, solubility, and mobility in the environment and living organisms. Cr(VI) is considered a carcinogen [6] and reflects toxicity toward many living organisms (plants, microorganisms, animals, etc.) [3–6]. The source of Cr(VI) in wastewaters is the effluents discharged from the industrial treatment [7]. The most cost-effective process for the removal of Cr(VI) from wastewater is the adsorption process [8].

Recently, the 2D carbon nanomaterials such as graphene oxide (GO) due to their extraordinary properties are also explored as adsorbents. GO is a product obtained from the chemical exfoliation and oxidation of layered graphite [9–13]. The adsorptive properties of GO are due to its huge surface area and the oxygenated functional

groups on its structure [10,11]. This material is ideal as an adsorbent in aqueous media as it is highly hydrophilic, forming stable aqueous dispersions. Theoretical studies are valuable and often applied to study carbon nanomaterials to better understand their interaction with different types of molecules or ions [14,15].

To experimentally put in evidence the adsorptive properties of GO toward the dichromate ions, AAS measurements were performed. After evaluating experimentally the adsorptive ability of GO, theoretical calculations based on density functional theory (DFT) and Monte Carlo (MC) were used to obtain molecular-level insights for better understanding this process.

2 Methods

2.1 Synthesis of GO

The GO synthesis is based on the procedure published by Abdolhosseinzadeh et al. [16]. One gram of graphite flakes was added to 50 mL of cooled concentrated sulfuric acid (stirred in an ice-water bath). Then, 3 g of potassium permanganate was gradually added carefully by keeping the temperature below 10°C. The formed suspension was stirred at room temperature for 25 min followed by 5 min sonication in the ultrasonic bath. After repeating the stirring–sonication process for 12 times, the reaction content is quenched by the addition of 200 mL of DI water. This solution is left for 2 h under ultrasonication. A 20 mL 30% hydrogen solution was added to the graphite oxide suspension and stirred until no gas evolution is observed. The GO was washed with 1 M hydrochloric acid solution and deionized water several times for 30 min each by centrifugation. The obtained GO precipitates are dried at room temperature.

2.2 Adsorption studies

For the evaluation of adsorptive properties of GO, 100 mL of dichromate solution (50 mg L⁻¹) was added into a 200 mL vessel with a fixed GO mass of adsorbent (0.015 g) and was agitated at a speed of 500 rpm at 25°C. The dichromate content of the solution is analyzed (after the adsorbent was separated from the samples by centrifugation and filtering) after 1–60 min by atomic absorption spectrometry (AAS).

The amount of adsorption q (mg kg⁻¹) is calculated as follows:

$$q = \frac{(C_{\text{init}} - C_{\text{eq}}) \times V}{m \times 1,000},$$

where C_{init} and C_{eq} are the initial concentration and equilibrium concentration of Cr(vi) ions, respectively (mg L⁻¹), V is the volume of aqueous phase (mL), and m is the mass (g) of GO.

The percentage of adsorption (%) can be calculated using the following equation:

$$\text{Ads. (\%)} = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{init}}} \times 100.$$

2.3 AAS measurements

AAS measurements were done using a High-Resolution Continuum Atomic Absorption Spectrometer with continuum light source – AAS Model novAA[®] 300 from Analytik Jena AG.

2.4 Computational details

Ab initio calculations were carried out with the DFT using the Dmol3 software. A previously employed GO model served for the adsorption study consisted of a 5 × 5 graphene layer (with epoxy, carboxy, and hydroxyl functional groups on its surface) [18]. The calculations were based on the triple-numeric quality with the polarization functions (TNP) basis set [19]. The exchange–correlation energy is described by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [18,20]. The van der Waals interaction on the calculations was accounted for using the Tkatchenko–Scheffler method [21]. Self-consistent-field (SCF) convergence criterion was set to the root-mean-square change in the electronic density to be less than 10⁻⁶ eV. All energy minima were characterized by performing a vibrational analysis to ensure the lack of imaginary frequencies [22,23].

The adsorption energy [14,18,23] was calculated as follows:

$$E_{\text{adsorption}} = E_{\text{GO/Cr(VI)}} - E_{\text{GO}} - E_{\text{Cr(VI)}},$$

where $E_{\text{GO/Cr(VI)}}$ is the total energy of the adsorption system. E_{GO} and $E_{\text{Cr(VI)}}$ are the energies of the isolated GO and Cr(vi) ions. The noncovalent interaction (NCI) was

computed using Multiwfn software [24]. The NCI surface is plotted using Visual Molecular Dynamics software [25].

The electron density difference (EDD) was calculated using Cambridge Sequential Total Energy Package software [26]. The geometry optimization is performed by using the GGA-PBE [18,20]. A norm-conserving pseudopotential was used for the calculations. The Broyden–Fletcher–Goldfarb–Shanno algorithm was applied for the optimization and EDD of the model, with the SCF tolerance set at 2.0×10^{-6} eV/atom.

2.5 MC calculations

For MC, the interaction is between dichromate ions and the surface of GO in the simulated adsorption aqueous media. The calculation was performed under periodic boundary conditions. For the simulation, one potassium dichromate + 100 water molecules (as a solvent) were used (the system charges were assigned using the charge equilibration [Q_{Eq}] method). The MC is performed by using several cycles of simulated annealing. During the annealing process, the temperature was set automatically at 10,000–100 K for each annealing cycle. The adsorption configurations were acquired as the temperature was slowly decreased. The Metropolis MC method was used to evaluate the adsorption configurations (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies – COMPASS II force field [27] [energy convergence tolerance of 2×10^{-5} kcal/mol and force convergence tolerance of 0.001 kcal/mol/Å]) of the interaction between the molecules and the substrates.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

Figure 1 presents the Fourier transform infrared spectroscopy (FTIR) spectra of GO.

The spectra of GO show the presence of bands related to C–O (ν_{C-O} at $1,050\text{ cm}^{-1}$), C–O–C (ν_{C-O-C} at $1,230\text{ cm}^{-1}$), C–OH (ν_{C-O-H} at $1,380\text{ cm}^{-1}$), and CO in carboxylic acid and carbonyl moieties that are present mostly along sheet edges but also on the basal plane of graphene sheets (ν_{CO} at $1,715\text{ cm}^{-1}$) and a broad peak between $3,000$ and $3,550\text{ cm}^{-1}$ corresponding to O–H vibration [13,28,29]. The UV-Vis spectra of GO are presented in Figure 2.

In water, the GO dispersion has a peak at around 232 nm, attributed to $\pi \rightarrow \pi^*$ transitions of aromatic C=C

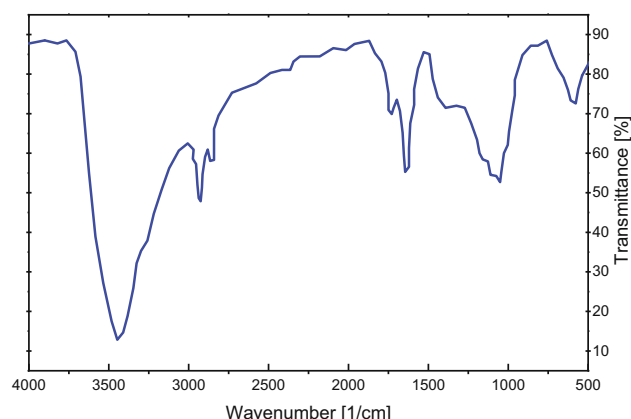


Figure 1: FTIR spectra of the synthesized GO.

bonds, and a peak at around 301 nm due to $n \rightarrow \pi^*$ transition of aromatic C=O bonds [13,30]. As evaluated by AAS, the adsorption of the Cr(VI) onto the GO is a fast process. The adsorption percentage after a short contact time ($t = 15$ min) reaches 73.15% ($q = 233.35\text{ mg/g}$), and this value almost remains the same regardless of the time interval up to 24 h, where this value is 74.12%. The same holds also for the adsorption capacity. In this case, the adsorption capacity value is $q = 240.361\text{ mg/g}$. A value that is in the same range as the GO/polyamidoamine dendrimer composites for the Cr(VI) adsorption [17].

From Figure 3, the adsorption energies for the Cr(VI) ion onto the GO surface are in the range from -133.7 to -143.8 kcal/mol depending on the adsorption site. The highest adsorption energy is obtained for the Pose_3, in which the dichromate ion (where its oxygen atom bonded between two Cr atoms) is located near the surface hydroxyl group of the GO.

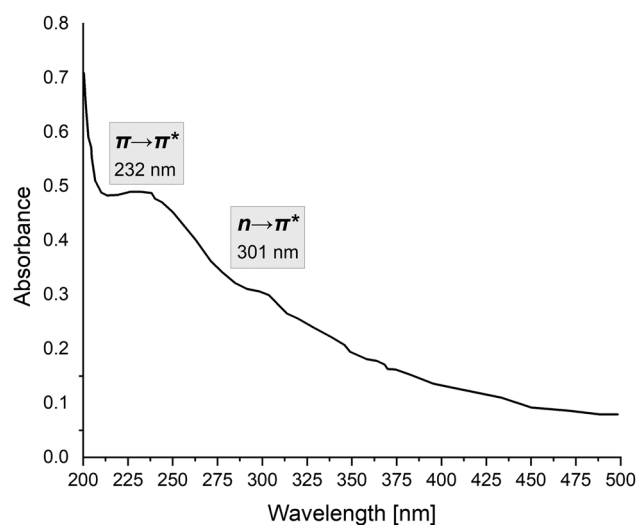


Figure 2: UV-Vis absorption spectra of GO in DI water.

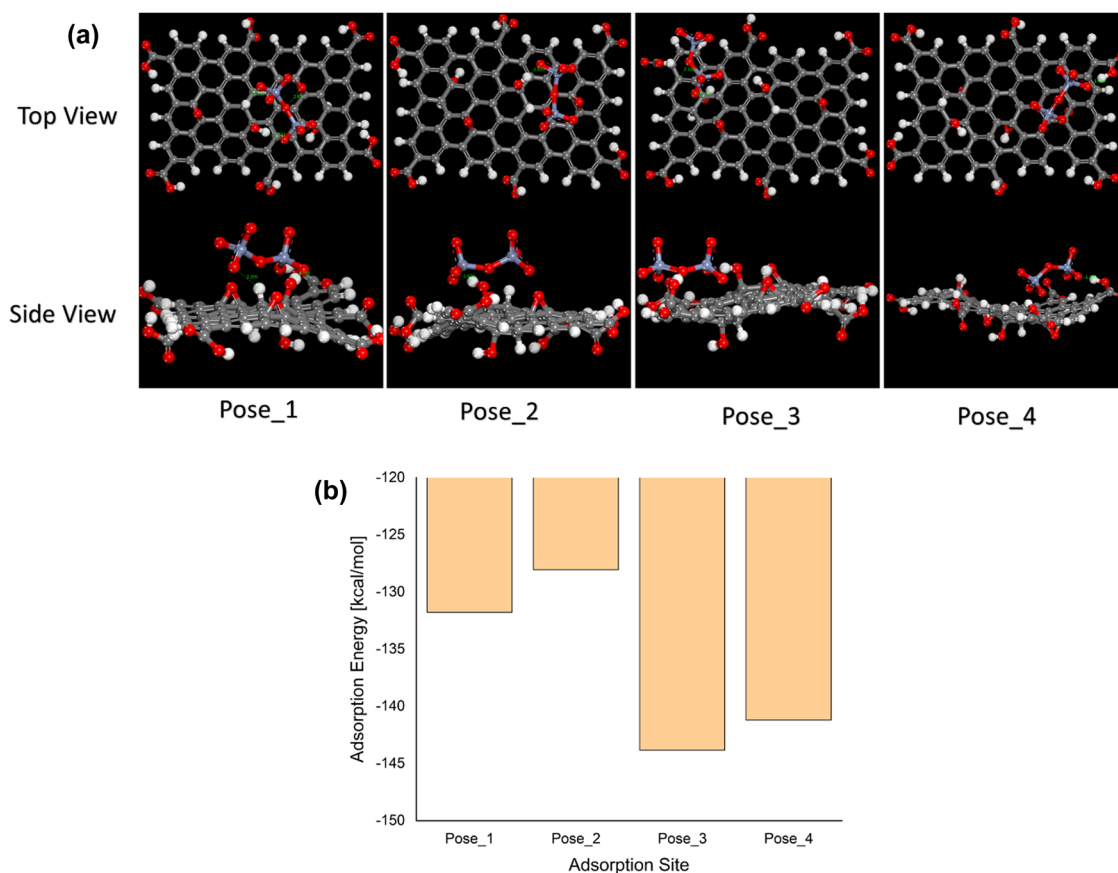


Figure 3: (a) Four different explored adsorption sites for the dichromate ion on the GO surface (the GO model is approximated by using a 5 × 5 graphene model that contains epoxy, hydroxyl, and carboxy groups on its surface) (level of theory: GGA/PBE/DFT-D = TS [Tkatchenko and Scheffler])//TNP – triple numerical polarized basis set; basis file: 4.4) and (b) the corresponding adsorption energy values.

To correctly assess the interaction type [14,22,23] between the chromate ions and GO surface, the NCI plot and the reduced density gradient (RDG) vs. $\text{sign}(\lambda)\rho$ were computed [31] for the highest adsorption site, in

this case, Pose_3. The visualization of the NCI surface (Figure 4(a)) and the RDG vs $\text{sign}(\lambda)\rho$ (Figure 4(b)) supports that the adsorption interaction is a van der Waals one.

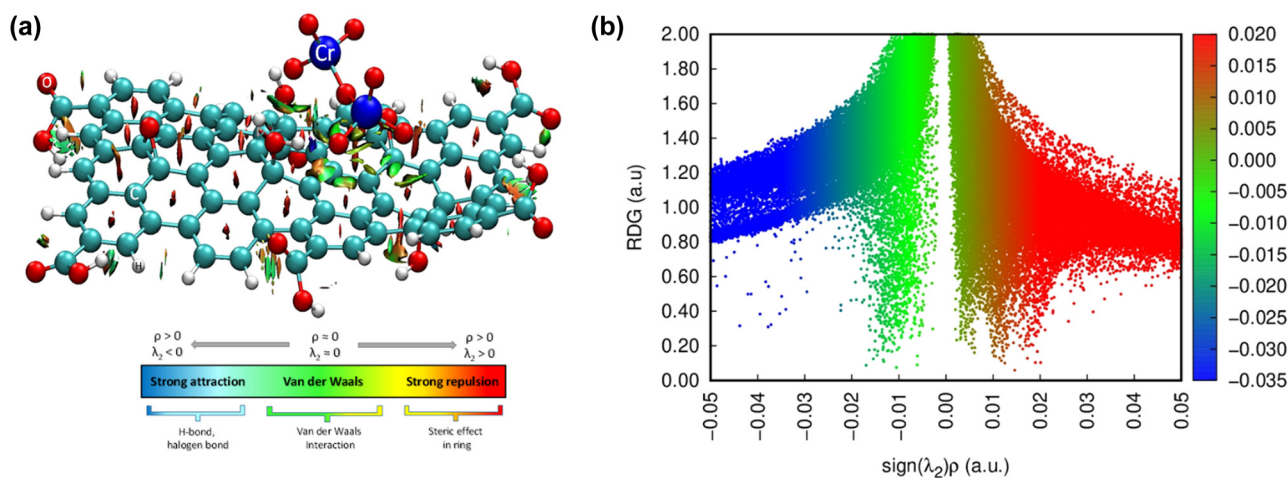


Figure 4: (a) Noncovalent interaction surfaces and (b) the plot of RDG vs $\text{sign}(\lambda)\rho$ for the interaction of GO/dichromate ion (Pose_3).

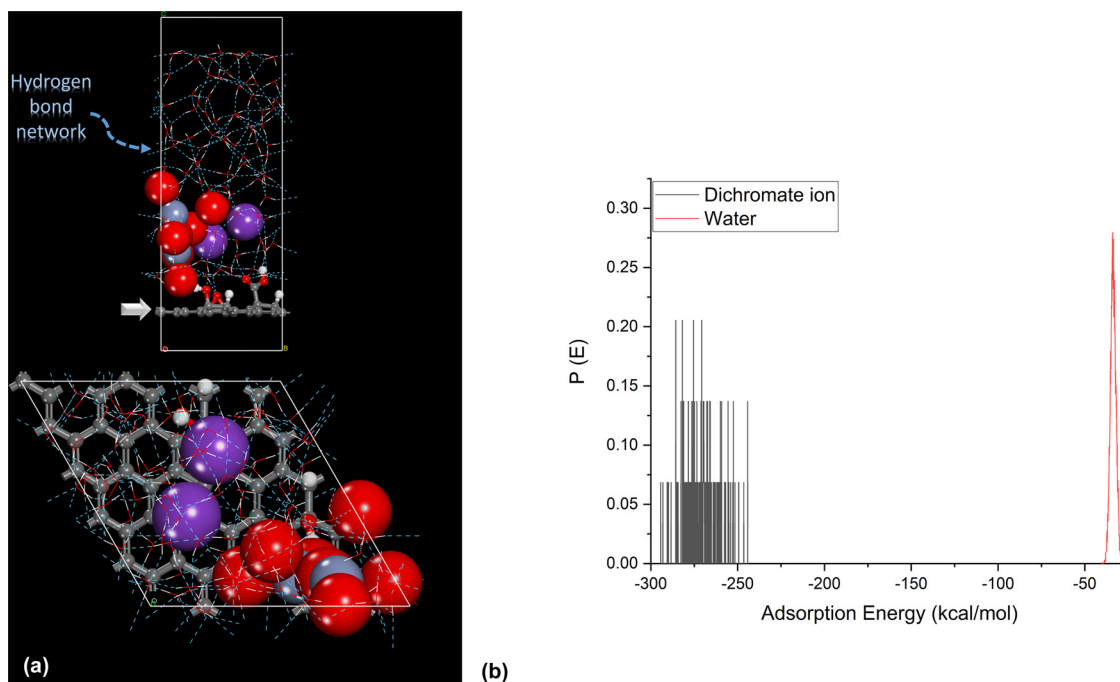


Figure 5: (a) Side and top views of the equilibrium adsorption configurations of the dichromate ions (one dichromate ion + 100 water molecules) onto the GO model (5×5 graphene layer containing: an epoxy, carboxy, and hydroxyl functional groups on its surface obtained using MC simulations) and (b) adsorption energy distributions for dichromate ions.

MC calculations are frequently used to understand the adsorptive properties of different molecular entities at the surface of materials [32,33], although this calculation is semi-quantitative. The adsorption geometry and energy distributions for the GO/Cr(VI)/100 H₂O system obtained by the adsorption locator module are presented in Figure 5.

As shown in Figure 5, the adsorption energy of Cr(VI) is $290.32 \text{ kcal mol}^{-1}$, which indicates the presence of strong adsorptive interaction between the GO surface and the Cr(VI). The adsorption energy values are comparable with those found in the previous studies (where a different and a smaller GO model is used) [34]. It is important to observe that as computed by DFT calculation, the preferred adsorption site of the Cr(VI) is also predicted by MC. This is associated with the fact that electrostatic interactions can take place at this adsorption site as found previously by Mondal et al. [34].

The EDD map of the adsorbed dichromate ion on the GO surface (Pose_3) is presented in Figure 6. The areas presented in yellow depict the increase (gain) of the electron density and those in blue depict the decrease (lost) among the interacting entities: GO and the dichromate ion. The electrons from the GO surface are transferred to the dichromate ion during the adsorption process. Electron increase and a decrease among oxygen atoms of

dichromate ion and the hydroxyl group support the electrostatic type of interaction among GO and dichromate ion.

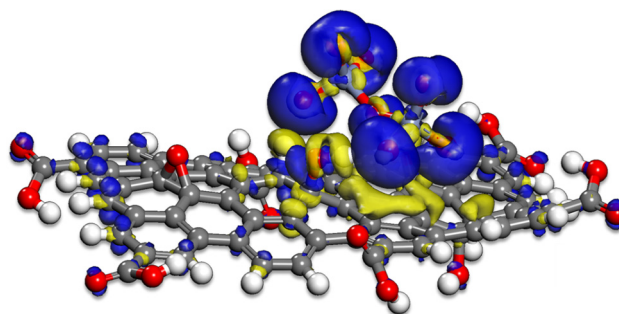


Figure 6: EDD for the adsorbed dichromate ion on the GO surface (Pose_3).

4 Conclusions

The adsorption of the Cr(VI) ions onto GO is explored both experimentally using AAS measurements and theoretically using DFT and MC calculations. The experimental results show that the GO has fast adsorption and high adsorption capacity toward the Cr(VI) ions.

The adsorption capacity is 240.3 mg/g, making GO a possible candidate for the application in the removal of this toxic chemical species. Furthermore, the high adsorption energy values as evidenced by theoretical calculation show that these ions strongly interact with the groups in the graphene surface, particularly with the hydroxyl ones.

The computed NCI surfaces point out that in the adsorption of these ions, an important role is played by van der Waals interaction. The EDD shows that the electrostatic interaction takes place where the dichromate ions attract the electron density from the GO surface. The present study not only puts in evidence the practical applicability of GO as an effective adsorbent for Cr(VI) ions but also gives molecular insights regarding the adsorption sites of GO, interaction type, and adsorption energetics of this material toward the toxic hexavalent chromium ions.

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Conflict of interest: The authors declare no conflict of interest.

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