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Impact of Selected Adsorbent Functional Groups on Chromium Sorption Capacities In An Effluent Treatment: A DFT Study

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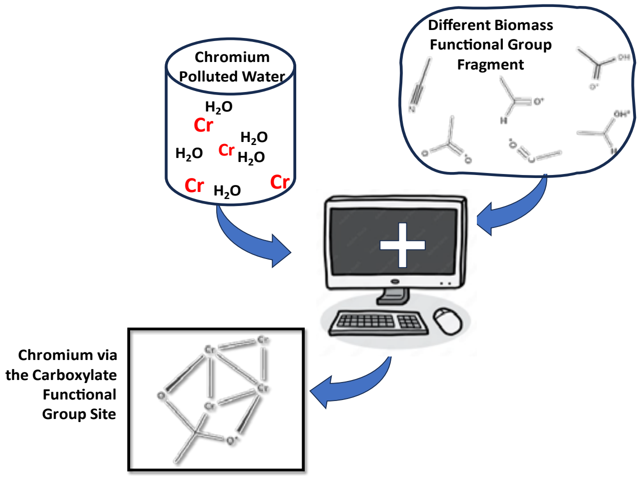

ABSTRACT: Communities are often exposed to high health risks via the presence of most heavy metals in water bodies used by their residents. Chromium, an abundant heavy metal in industrial effluents, contaminates our environment and water sources, endangering human and animal consumption. Designing materials for Cr removal from potential effluent discharges is crucial. Bio-based sorbents have been explored, but the role of functional groups remains unclear. This research investigates the influence of functional groups in removing dissolved chromium heavy metals to enhance water quality. In this study, we look at how well functional groups like carboxylate, carbonyl, nitrile, aldehyde, alcohol, and carboxylic acid bind to Cr (III) metal. We look at stable Cr metal cluster configurations using Spartan software and density functional theory (DFT) for quantum chemical calculations. We measure energies and thermodynamic properties during interactions. Our findings demonstrate that sorbents with carbonyl and carboxylate groups exhibit high sensitivity to Cr, making them effective for removal. The relative adsorption energies align with experimental results. This study confirms the potential of computational methods to predict sorbents' selectivity in removing various heavy metals from water, offering a promising avenue for water treatment and environmental protection.

Keywords: Density functional theory; Effluent treatment; Environmental protection; Metal sorption; Modelling; Simulation.

تأثير المجموعات الوظيفية للممتصات المختارة على قدرات امتزاز الكروم في معالجة المخلّفات: دراسة باستخدام نظرية الكثافة الوظيفية

تويزي أويغوك, عليو عدنان

الملخص: تتعرض المجتمعات لمخاطر صحية عالية بسبب وجود معظم المعادن الثقيلة في المسطحات المائية التي يستخدمها سكانها. يُعد الكروم، وهو معدن ثقيل وفير في المخلّفات الصناعية، ملوثًا للبيئة ومصادر المياه، مما يشكل خطرًا على استهلاك الإنسان والحيوان. يُعد تصميم مواد لإزالة الكروم من تصريفات المخلّفات المحتملة أمرًا بالغ الأهمية. تم استكشاف الممتزات القائمة على المواد الحيوية، لكن دور المجموعات الوظيفية لا يزال غير واضح. تبحث هذه الدراسة في تأثير المجموعات الوظيفية في إزالة المعادن الثقيلة المذابة من الكروم لتحسين جودة المياه. في هذه الدراسة، ننظر في مدى ارتباط المجموعات الوظيفية مثل الكربوكسيلات، الكربونيل، النتريل، الألدهيد، الكحول، وحمض الكربوكسيل مع معدن الكروم (III). ندرس تكوينات تجمعات معدن الكروم المستقرة باستخدام برنامج Spartan ونظرية الكثافة الوظيفية (DFT) لحسابات الكيمياء الكمومية. نقيس الطاقات والخصائص الديناميكية الحرارية أثناء التفاعلات. تُظهر نتائجنا أن الممتزات ذات مجموعات الكربونيل والكربوكسيلات تتميز بحساسية عالية للكروم، مما يجعلها فعالة للإزالة. تتماشى طاقات الامتزاز النسبية مع النتائج التجريبية. تؤكد هذه الدراسة على إمكانات الأساليب الحسابية في التنبؤ بانتقائية الممتزات في إزالة المعادن الثقيلة المختلفة من المياه، مما يوفر طريقًا واعدًا لمعالجة المياه وحماية البيئة.

الكلمات المفتاحية: نظرية الكثافة الوظيفية؛ معالجة المخلّفات؛ حماية البيئة؛ امتزاز المعادن؛ النمذجة؛ المحاكاة.

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1. INTRODUCTION

The escalating discharge of toxic materials into our environment has become a pressing concern that demands immediate attention (Jessica et al., 2020). These hazardous substances, whether in gas, liquid, or solid form, contribute significantly to air, water, and land pollution. Industries often release such materials into the environment through flare gas, solid waste, or effluents, posing threats to human, plant, and animal life in ecosystems (Tchounwou et al., 2012; Jaishankar et al., 2014).

Focusing on water pollution, a literature review reveals the extent of toxicity to which our community is exposed, primarily through industrial effluents. Industries such as textiles, tanneries, metallurgy, mining, petroleum, petrochemicals, and others discharge harmful effluents containing dyes, heavy metals, toxic chemicals, and various water-based pollutants (Sathya et al., 2022). This study specifically addresses the elimination or reduction of heavy metals from industrial effluents, including zinc, iron, copper, vanadium, nickel, chromium (Staszak et al., 2022), cadmium, and others.

Previous research has explored different strategies and materials to convert these toxic effluents into less harmful substances. This conversion is crucial for establishing pretreatment units in industries before discharging effluents into the environment. Methods such as absorption, adsorption, Fenton oxidation, ion exchange, membrane separation, and others have been investigated (Puszkarewicz & Kaleta, 2019; Sathya et al., 2022; Staszak et al., 2022). In the context of chromium metal removal, the focus of this study, various approaches and materials have been explored using both experimental and computational methods.

Literature reviews (Puszkarewicz & Kaleta, 2019; Sathya et al., 2022; Staszak et al., 2022) indicate that some works have concentrated on synthesizing activated carbon, zeolites, biosorbents, graphene, and adsorption-based materials. However, these studies often overlook the role of functional groups in the adsorption process. While some works identify the functional groups present, they struggle to experimentally explain how these functions influence the performance of their adsorbents or sorbents in metal removal. Previous studies by our team have demonstrated the significant role of functional groups in removing cadmium and barium metals (Oyegoke et al., 2023; Aliyu et al., 2023), aligning well with experimental reports. Nonetheless, there is a gap in understanding how this applies to other heavy metals, such as chromium, commonly found in textile effluents.

In this study, we investigated the impact of functional groups, commonly found on experimentally synthesized adsorbent surfaces, on the removal of chromium (Cr) from effluent water through adsorption processes.

In our analysis, we computationally explored the influence of these functional groups using B3LYP-D3 dispersion-corrected density functional theory calculations (to ensure accurate long-range interaction calculations, including the D3 dispersion correction method) and solvation effects to account for the presence of solvent (water) in the system. In a nutshell, our investigation focused on elucidating the role of each functional group in the presence of water, specifically considering the aqueous form of the adsorption process. Chromium in this study refers specifically to Cr(III), and all mentions of 'Cr' denote Cr(III) throughout this report.

2. MATERIALS AND METHODS

2.1 Materials & Software

In this study, the Spartan v20/v24 package was used for molecular modelling and simulation of the adsorption studies. It was developed by Wavefunction Inc. US. Microsoft Excel package is also used for mathematical analysis and representation of data collated. Other resources used were journal articles and internet database information showing casing experimental data to compare our studies within the literature.

2.2 Computational Methods

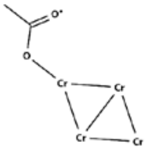
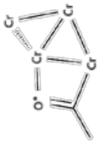
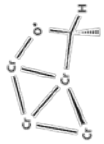
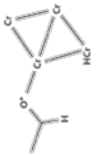
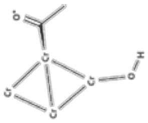
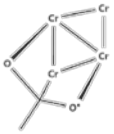
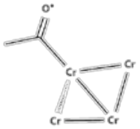
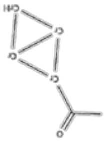
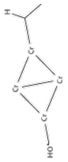
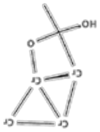
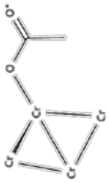
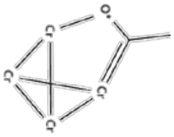
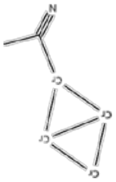
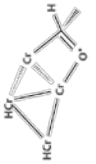
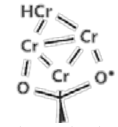
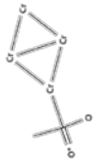
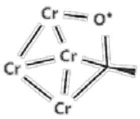
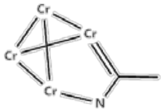
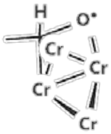
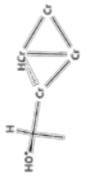
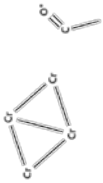
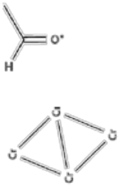
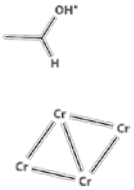
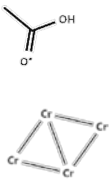
2.2.1 Structural Geometry Optimization

The molecular structures for the respective species involved in this study were built, modelled, and simulated in Spartan v20/v24. The structural geometry optimization of species modelled in this study was carried out using a vacuum B3LYP-D3 (Becke-style 3-Parameter functional - Grimme's dispersion) dispersion-corrected density functional theory calculation approach (Grimme et al., 2011; Becke, 1993;). The choice of the method was in line with the literature report that confirms that it is effective for efficiently computing energies involving a long-range non-interaction, better than the old way of employing B3LYP (Torres and DiLabio, 2012) without a dispersion correction component in its energy calculation.

2.2.2 Energy and Frequency Calculations

The calculations of the single-point energy and frequency using B3LYP-D3 DFT calculation in the presence of solvent (water) were deployed to improve the accuracy of the resulting energy to enable to it take into account the solvation effect to mimic the aqueous form in which the industrial effluent would always be. In the calculations, 6-31G* basis set and Van der Waal radius (PCMRAD) of Chromium (Cr)~1.3608A, Oxygen (O)~1.52A, Carbon (C)~1.92A, Hydrogen (H)~1.2A, and Nitrogen (N)~1.55A were employed in the solvated and dispersion-corrected energy calculation.

Table 1. Different adsorption mechanisms for the metal and sorbent fragment's functional groups interaction.

Cr+COO	Cr+CO	Cr+CN	Cr+CHO	Cr+COH	Cr+COOH
 CrCOO1 1 singly bonded Cr-O	CrCO1  2 singly bonded Cr-O, Cr-C	CrCN1  2 singly bonded Cr-N, Cr-C	CrCHO1  2 singly bonded Cr-O, Cr-C	CrCOH1  1 singly bonded Cr-O	CrCOOH1  1 singly bonded Cr-C
CrCOO2  3 singly bonded 2 Cr-O, Cr-C	CrCO2  1 singly bonded Cr-C	CrCN2  1 singly bonded Cr-N	CrCHO2  Dissociative HCr-CrC	CrCOH2  Dissociative HOCr-CrC	CrCOOH2  2 single bond Cr-O, Cr-C
 CrCOO3 1 singly bonded, Cr-O	CrCO3  1 singly and 1 doubly bonded Cr-O, Cr=C	CrCN3  1 singly bonded Cr-C	CrCHO3  Dissociative HCr-CrO	CrCOH3  Dissociative (HCr)HCr-CrC(CrO)	CrCOOH3  Dissociative HCr-CrO(CrO)
CrCOO4  1 singly bonded, CrC	CrCO4  3 singly bonded 2 Cr-C, Cr-O	CrCN4  1 singly and 1 doubly bonded Cr-C, Cr=N	CrCHO4  2 singly bonded Cr-O, Cr-C	CrCOH4  1 singly bonded Cr-C	CrCOOH4  1 singly bonded, Cr-C
CrCOO0  Non-bonded	CrCO0  Non-bonded	CrCN0  Non-bonded	CrCHO0  Non-bonded	CrCOH0  Non-bonded	CrCOOH0  Non-bonded
CrCOO5  2 singly bonded, 2 Cr-O	Nil	Nil	Nil	Nil	Nil

The resulting energy value obtained for taking into account the dispersion and solvation effect in the energy calculation was labelled as “B3LYP-D3+SOL”, while ones with only the dispersion effect (without solvation effect) were labelled as “B3LYP-D3” in our results presentations.

2.2 Study Strategy

In this study, the strategy involved the exploration of the different functional groups' influence on the interaction of the chromium metals with sorbent/adsorbent fragments. These models are presented in Tables 1 and 2. Table 1 presented the different forms of possible sorption/adsorption mechanisms of how each of the functions could possibly interact with the metal on the sorbent/adsorbent surface. The different form of the interaction mechanism includes the non-bonded interaction (or physisorption), dissociative adsorption, molecular adsorption via singly bonded, two singly bonded, singly and doubly bonded, and three singly bond interactions. Other details for the interaction mechanism are as follows:

2.2.1 Carboxylate (COO)

Interaction of Cr with these functional groups as shown in Table 1 below has a nomenclature ranging from CrCOO0 to CrCOO5 indicating the different adsorption modes. CrCOO0 has a non-bonded interaction; CrCOO1 has a single bonded interaction of Cr-O; CrCOO2 has a three single bonded interaction of two Cr-O and Cr-C; CrCOO3 has a single bonded interaction of Cr-O; CrCOO4 has a single bonded interaction of Cr-C and CrCOO5 has a two single bonded interaction of two Cr-O. However, CrCOO1 and CrCOO3 seem to be similar but the former (-COO) interact with less saturated Cr, while the latter (-COO) interact with more saturated Cr in Table 1.

2.2.2 Carbonyl (CO)

Nomenclature of Cr-CO Interactions ranges from CrCO0 to CrCO4 indicating different adsorption modes. CrCO0 has a non-bonded interaction; CrCO1 has two single bonding of Cr-O and Cr-C; CrCO2 has a single bonded interaction of Cr-C; CrCO3 has one single and one double bonding interaction of Cr=C and Cr-O; and CrCO4 has three single bond interaction involving one Cr-O and two Cr-C.

2.2.3 Nitrile (CN)

Cr-CN Interactions has a nomenclature ranging from CrCN0 to CrCN4 indicating different adsorption modes. CrCN0 has a non-bonded interaction; CrCN1 has two single bonded interactions of Cr-N and Cr-C; CrCN2 is a dissociative adsorption mechanism where hydrogen ion from nitrile molecule got attracted by a chromium atom from the cluster; CrCN3 has a single bonded interaction of Cr-C; and CrCN4 has a single and double bonded interaction of Cr-N and Cr=C but, CrCN1 and CrCN4 seems to be similar but the later mechanism do have nitrogen (-N) with less saturation.

2.2.4 Aldehyde (CHO)

Cr-CHO Interactions has a nomenclature ranging from CrCHO0 to CrCHO4 indicating different adsorption modes. CrCHO0 has a non-bonded interaction; CrCHO1 has two single bonded interactions of Cr-C and Cr-O; CrCHO2 has dissociative adsorption with *H elimination; CrCHO3 has dissociative adsorption with *H elimination; and CrCHO4 has a two single bond interaction via Cr-O and Cr-C.

2.2.5 Alcohol (COH)

Cr-COH Interactions have a nomenclature ranging from CrCOH0 to CrCOH4 indicating different adsorption modes. CrCOH0 has a non-bonded interaction; CrCOH1 has 2 single bonded interactions of Cr-O and Cr-C; CrCOH2 has dissociative adsorption with *OH elimination; CrCOH3 has dissociative adsorption with *H elimination; CrCOH4 has a singly bonded interaction of Cr-C.

2.2.6 Carboxylic acid (COOH)

Cr-COOH Interactions have a nomenclature ranging from CrCOOH0 to CrCOOH4 indicating different adsorption modes. CrCOOH0 has a non-bonded interaction; CrCOOH1 has a single bonded interaction of Cr-C; CrCOOH2 has a two single bonded interaction of Cr-C and Cr-O; CrCOOH3 has dissociative adsorption with *H elimination; CrCOOH4 has a singly bonded interaction of Cr-C.

2.3 Adsorption Strength (Eads) and Gibbs Free Energies Calculations

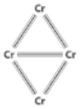
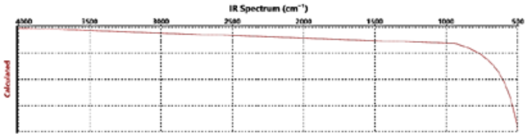
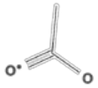
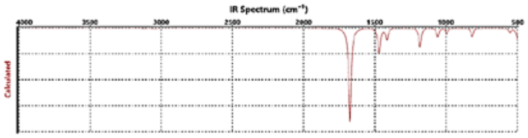
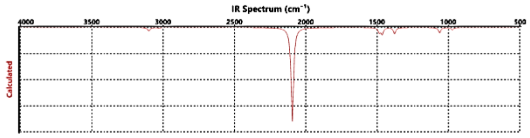
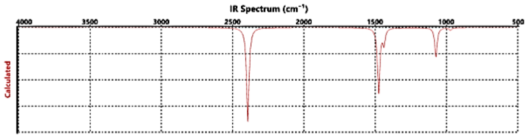
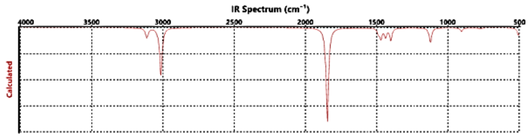
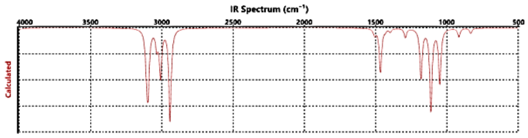
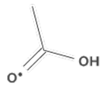
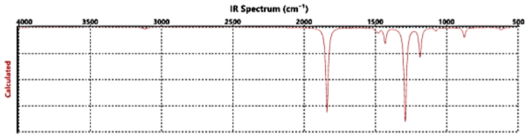
In the study, the use of the adsorption strength (Eads) and the adsorption Gibbs free energies (ΔGads) were deployed in identifying the thermodynamically feasible adsorption mechanism (Oyegoke et al., 2023; Aliyu et al., 2023) for each functional group explored in this study using Equation I and II. Using relevant molecular properties obtained from the DFT calculation, an inbuilt statistical thermodynamic model in Spartan 20/24 was deployed for the computation of the Gibbs free energies at standard temperature (298.15K) and pressure (1 atm) used in the calculation of the adsorption Gibbs free energies (ΔGads) in Equation II

$$Eads = Eax - Ea - Ex \quad (1)$$

$$\Delta Gads = Gax - Ga - Gx \quad (2)$$

Where Ea, Ex, and Eax are the metal’s electronic energy, the adsorbent or sorbent material’s electronic energy, and the electronic energy of the bonded form of the metals-adsorbent structure, respectively. Similarly, Ga, Gx, and Gax are the Gibbs free energy versions of the metals, adsorbent, and metal-adsorbent structure.

Table 2. Infrared Spectra for The Cr Metal and Other Functional Fragment of the Adsorbent.

Species	Structure	IR Spectra	Compt Vib Freq.	Expt./Lit. Freq.
Cr4		 F	>500	3451–3500^b ~4000–400^c
-COO			1675	1610–1550^a
-CO			2094	2100–1800^a
-CN			2393	2280–2240^a
-CHO			1846	1740–1725^a
-COH			2900-3100 1050-1550	3400-3200^a ~1200-1050
-COOH			1291 1839	1725–1700^a

3. RESULTS AND DISCUSSIONS

3.1 Model Validation for The Simulations (Spectra Prediction with Experiments)

Fourier Transform Infrared (FTIR) as an analytical technique is used to characterize all chemical species involved in this study, in terms of specific molecular vibrations evaluated in our study. Table 2 presents the set of results showing the comparison of our theoretically computed vibration frequencies with the ones experimentally collated in the literature to justify the validity of our chosen model for the metal and the functional fragments of the adsorbent in our study.

Alcohol-based fragment (-COH) with two different peaks behaved like primary alcohol with C-O stretch at a lower frequency while at a higher frequency was a normal polymeric stretch. Aldehyde-based fragment (-CHO) with a single peak was a C-H stretch. Acid-based fragment (-COOH) was found to be a C-O stretch similar to transition metals carbonyl. Nitrile/cyanide-based fragment (-CN) vibration was similar to that of an aliphatic cyanide. Findings for the comparison of the peaks obtained for both the experiment and theoretically computed one show that all the atomic computed vibrations for the chemical species models agreed with experimentally collated data as shown in Table 2 with negligible difference (Nandiyanto et al., 2019; Mart et al., 2023; Andrei et al., 2006).

3.2 Analysis of The Model's Molecular Properties

Quantum chemical parameters such as HOMO energy (E-HOMO), LUMO energy (E-LUMO), energy gap (E-Gap), Electronegative, chemical softness or hardness are measures that describe the electronic properties of molecules in DFT calculations (Bello et al., 2019; Usman et al., 2019). In this study, we evaluated these aforementioned properties, which are presented in Table 3. The properties are used to evaluate how each of the functional groups considered herein interacts with Cr. However, all properties considered here were carried out using dispersion-corrected DFT with the solvation (H2O) effect.

Table 3. Molecular Properties of Functional Biomass Fragments and Metal Model

Species	E-Gab (eV)		E-HOMO (eV)		E-LUMO (eV)		HARDNESS		ELECTRONEG.	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr4	1.63	1.91	-3.85	-2.42	-2.23	-0.50	0.81	0.96	3.04	1.46
-COO	8.53	8.69	-8.87	-8.95	-0.34	-0.26	4.26	4.34	4.61	4.60
-CO	3.83	3.91	-4.35	-4.40	-0.53	-0.48	1.91	1.96	2.44	2.44
-CN	9.84	9.96	-8.86	-9.00	0.98	0.97	4.92	4.98	3.94	4.01
-CHO	6.35	6.45	-6.92	-6.97	-0.58	-0.52	3.17	3.23	3.75	3.75
-COH	9.31	9.73	-7.14	-7.16	2.17	2.57	4.66	4.87	2.48	2.30
-COOH	7.40	7.67	-7.19	-7.44	0.20	0.23	3.70	3.84	3.50	3.61

Following the report of the literature (Radhi et al., 2020; Ibrahim et al., 2020), the energy gap (E-Gap) is the difference between the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which is a measure of the chemical reactivity and stability of a molecule. Cr has displayed a very reactive behaviour looking at the lower E-gap which shows its availability for ion exchange or interaction with other molecules which is similar to the findings in the literature (Toyese et al., 2020), which reports that Cr is highly reactive. Among all the functional fragments evaluated, nitrile (-CN), carboxylate (-COO), and alcohols (-COH) show a wider energy gap indicating less reactive and more stable, while chromium metal species (Cr4) showed a shortest energy gap and can said to be more reactive and less stable, following the trend of their respective energy gaps. This confirms that species with the nitrile (-CN), carboxylate (-COO), and alcohols (-COH) functions are found to have shown highest hardness, while chromium metal species (Cr4) showed the least hardness and highest Electronegative. According to the hard and soft acid-base (HSAB) principle, a molecule with a small value of global hardness (η) and large value of softness (S) is expected to have the high intensity of interaction (Usman et al., 2019). In this regard, the Cr cluster showed the least chemical hardness and higher Electronegative (similarly to chemical softness), while the functional fragment with nitrile (-CN), carboxylate (-COO), and alcohols (-COH) has higher chemical hardness as shown in Table 3. This suggests that the Cr (with strong Electronegative to accept electrons)would best interact with either -COO, -CN, or -COH (with strong chemical hardness) have shown an exciting level of flexibility in solvation and non-solvation medium.

HOMO energy (E-HOMO) is often associated with the electron-donating ability of a molecule. specie (Cr4) shows the least negative energy value (-3.85 eV), while specie (-COO) shows the highest negative value (-8.87 eV). This implies that Specie (-COO) with the highest negative E-HOMO value would have the highest tendency of donating electrons to another molecule/material like chromium metals. Whereas, the LUMO energy (E-LUMO) is the electron acceptability of a molecule. A highly negative value of E-LUMO like Specie (Cr4 i.e., the chromium metals) indicates the tendency to accept electrons from other materials like the functional fragment species, in agreement with the literature (Oyegoke et al., 2018; 2021). They suggest that the interaction process is more feasible for the species (Cr4) as the electron acceptor to interact better with the species (-COO) as the electron donor. In the presence of the solvation effect, the interaction earlier found to be feasible for specie(Cr4) and specie(-COO) was confirmed to become stronger in solvation medium (water) due to the highest electron donation capacity of specie(-COO) due to the higher negative value and the highest electron acceptor capacity of specie(-COO) showing higher negative value, when compared to other functional fragments.

3.3 Influence of Different Functional Groups on the Chromium Removal

The thermodynamic feasibility using adsorption Gibbs free energy (ΔGads) and interaction adsorption strength (Eads) of several functional groups like aldehyde (-CHO), carbonyl (-CO), nitrile (-CN), carboxylate (-COO), alcohol (-COH), and carboxylic acid (-COOH) interacting with chromium (Cr) metal has been presented in Tables 4 to 9 in order to gain more insight on the viability of chromium (Cr) metal removal in water.

3.3.1 Carboxylate Function in the Removal Process

This functional group is predicted to have high feasibility for reactivity in favouring the removal of Cr metal in water as it shows remarkable adsorption strengths and Gibbs free energies irrespective of the adsorption modes as revealed in Table 4.

Additionally, the solvation effect was noticed in CrCOO1 and CrCOO0, the latter can be attributed to a non-bonded physical interaction also known as physisorptive interaction between Cr and COO while the former could be due to the Cr-O double bonded interaction mode. The Gibbs free energy has shown a high thermodynamic feasibility in all the adsorption modes due to the highly negative Gibbs energy which suggests CrCOO2 (three singly bonded via two Cr-O and one Cr-C) mode of interaction involving two Cr-O and one Cr-C bonds to be most feasible and highly exergonic interaction via the carboxylate functions.

This finding indicates that acidic treatment such as that with carboxylates will favour chromium metal adsorption (Qi et al., 2017; Yang et al., 2019), which might be due to the presence of two (2) highly electronegative oxygen atoms.

3.3.2 Carbonyl Function in the Removal Process

The evaluated Cr-CO interaction mechanisms are presented in Table 5, with and without the presence of solvation effects. Analysis of the solvated energies for the various interaction mechanisms reveals that CrCOO0 (non-bonded interaction mechanism) exhibits the least adsorption strength, featuring the weakest mode of interaction between Cr and the (-CO) species, while CrCO3 and CrCO4 demonstrate the strongest adsorption strength compared to other interaction mechanisms.

Table 4. Feasibility of Carboxylate function (NaN indicates no results found at the studied conditions for those interactions as shown above).

Cr+COO	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+COO5	-13.96	-13.36	-13.28	-12.68
Cr+COO1	-12.83	-7.61	-12.19	-6.98
Cr+COO2	-13.99	-13.46	-13.32	-12.78
Cr+COO3	-13.33	-13.46	-12.64	-12.79
Cr+COO4	-12.26	-12.84	-11.62	-12.19
Cr+COO0	NaN	-7.31	NaN	-7.05

Table 5. Feasibility of Carbonyl function (NaN indicates no results found at the studied conditions for those interactions as shown above).

Cr+CO	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+CO1	-11.18	-10.35	-10.66	-9.82
Cr+CO2	-6.61	-9.99	-6.34	-9.76
Cr+CO3	NaN	-10.66	NaN	-10.16
Cr+CO4	-7.55	-10.6	-7.01	-10.07
Cr+CO0	-10.68	-6.41	-10.17	-5.93

The thermodynamic analysis of the various mechanisms showed that CrCO3 (singly and doubly bonded interaction via Cr-O and Cr=C, that is, Eads = -10.66 eV and ΔGads = -10.16 eV) and CrCO4 (three singly bonded interaction via two Cr-C and one Cr-O, that is, Eads = -10.6 eV and ΔGads = -10.07 eV) mechanism were the most feasible interaction mechanism found to be exergonically feasible due to their higher value of negative Gibbs adsorption energies taking solvation effect into consideration. This implies the feasible mode of interaction involves the interacting Cr with species(-CO) via Cr-O and Cr-C or Cr=O. Furthermore, high adsorption of Cr metal with carbonyl-rich chemical substances has been demonstrated by the findings in literature irrespective of the adsorption mode (Togibasa et al., 2021), where carbonyl compound was studied and found to be one of the functional groups that improve the adsorptive properties of biomass pore surfaces in general. Therefore, carbonyl functional groups will serve as criteria for selecting a good chemical activator in the synthesis of adsorption for Cr removal as it agrees with the findings in (Supong et al., 2022) due C-O bond, similar to the case of carboxylate function reported earlier in this report.

3.3.3 Nitrile Function in the Removal Process

The Cr-CN interaction strength generally showed a less promising and lower thermodynamic feasibility due to the low adsorption energy and Gibbs free energy reported for the mechanism in Table 6. Nonetheless, the solvation effect was noticed in the result to have facilitated or improved interaction strength and further improved its exergonicity (or feasibility) due to the increase in the negativity of the adsorption energy and Gibbs free energy, across all its adsorption mechanism modes. To specific, the CrCN3 mechanism which involves a singly bonded interaction via Cr-C showed the best adsorption strength (Eads = -3.38 eV) and exergonicity (ΔGads = -2.96 eV).

Table 6. Feasibility of Nitrile function

Cr+CN	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+CN1	-2.70	-3.01	-2.17	-2.50
Cr+CN2	-1.42	-2.03	-1.13	-1.77
Cr+CN3	-2.88	-3.38	-2.44	-2.96
Cr+CN4	-2.67	-2.79	-2.13	-2.27
Cr+CN0	-1.76	-2.32	-1.44	-2.06

A survey of literature (Zhao et al., 2021) has revealed similar findings made from the study of the amination reaction surface of low-cost bio-materials to enrich its amino-function content, which was reported to have improved bio-sorbent capacity for the adsorption of Cr, which successfully result to a higher reduction of Cr concentration in wastewater, this is to say that specie with this function (-CN) cannot be used to generalize all nitrogen-containing molecules as the case presented in this study. However, it could be deduced that the presence of -CN significantly improve the adsorption capacity, especially in an aqueous state, contrary to the case of other functions like -COO and -CO which get reduced in water.

3.3.4 Aldehyde Function in the Removal Process

In Table 7, we present the result collated for the adsorption strength and Gibbs free energy obtained from our computational analysis of aldehyde (-CHO) function in the treatment of wastewater containing Cr metals. Energies obtained for the solvation-free (using B3LYP-D3) and the solvation (B3LYP-D3+SOL) effect, which accounts for the water effect are presented in Table 7.

Similar to the findings made for the presence of function (-CN) in the earlier analysis, the aldehyde function (-CHO) was found to have shown a more significant effect when exposed to water (that is when the solvation effect is introduced), contrary to the reaction of carboxylate (-COO) and carbonyl (-CO) which shows a drop in their adsorption activity.

Table 7. Feasibility of Aldehyde function

Cr+CHO	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+CHO1	-2.70	-3.02	-2.14	-2.47
Cr+CHO2	-0.82	-1.47	-0.51	-1.21
Cr+CHO3	-1.97	-2.63	-1.58	-2.27
Cr+CHO4	-3.19	-3.99	-2.73	-3.58
Cr+CHO0	-0.21	-0.05	0.32	0.50

Exception of CrCHOO0 mechanism that shows a drop in its activity. Moreover, out of the various mechanisms explored for the use of the aldehyde (-CHO) function, the CrCHO4 (involving two singly bonded via Cr-O, Cr-C with Eads = -3.99 and ΔGads = -3.58) mechanism was found to have shown a better effect and hence confirming its to be the feasible mechanism for the adsorption Cr via the use of aldehyde (-CHO) functions. The better interaction obtained for the use of aldehyde (-CHO) function to remove Cr in water agreed with a report (Rajendram et al., 2016) in the literature which indicates that aldehydes are highly reactive metabolites having high affinity with water molecules and are also very toxic upon human consumption just like Cr metal.

3.3.5 Alcohol Function in the Removal Process

Here, we further present our findings for the use of alcohol (-COH) function in the chromium removal process in Table 8, carried out in the presence of water (B3LYP-D3+SOL) and without water (B3LYP-D3). The results include the presentation of adsorption energies and the adsorption Gibbs free energies.

The findings from the results presented in Table 8 reveal that CrCOH0 exhibits the least adsorption strength and exergonicity, whereas CrCOH2 and CrCOH3 demonstrate the highest adsorption strength and exergonicity, indicated by their more negative values for adsorption energy and Gibbs free energy. This suggests that the adsorption mechanism involved in chromium removal using the alcohol (-COH) function entails dissociative adsorption, resulting in either the abstraction of *H or *OH, as depicted in Table 1. This is in contrast to other functions, which have been reported to involve molecular adsorptions with single or multiple bond interactions. Additionally, the presence of water (i.e., the solvation effect) further enhances the interaction strength of the function with the chromium metal.

Table 8. Feasibility of Alcohol function

Cr+COH	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+COH1	-2.98	-3.26	-2.57	-2.88
Cr+COH2	-4.56	-4.73	-4.27	-4.48
Cr+COH3	-3.97	-4.92	-3.90	-4.89
Cr+COH4	-1.45	-2.15	-1.24	-1.98
Cr+COH0	-1.71	-1.90	-1.44	-1.66

However, a much lower strength was reported for using the alcohol function according to this analysis relative to other functions evaluated in this study. The advantage of its improved performance in water must favour that positive outcome often reported for its usage in laboratory experimental studies, according to the literature report showing its deployment by many researchers via the use of alcohols (Baldermann et al., 2020) or sodium hydroxide which contains the OH functional group as an alkaline for the adsorption of Cr and many other heavy metals in water using activated carbon or metallic oxides with positive outcome (Baldermann et al., 2018; Farooq et al., 2022).

3.3.6 Carboxylic Acid Function in the Removal Process

Based on the findings presented in Table 8 regarding the assessment of the carboxylic acid function in chromium metal removal, the results indicate a significant enhancement in the presence of water (i.e., the solvation effect).

This conclusion supports the notion that the removal of the metal is more favourably achieved in an aqueous form, despite exhibiting lower exergonicity and strength compared to other functions such as carboxylate (-COO) and carbonyl (-CO). These latter functions demonstrate a much stronger interaction strength in the removal of the metal than the carboxylic acid function.

Table 9. Feasibility of Carboxylic Acid functions

Cr+COOH	Eads (eV)		ΔGads (eV)	
	B3LYP-D3	B3LYP-D3+SOL	B3LYP-D3	B3LYP-D3+SOL
Cr+COOH1	-3.22	-3.60	-2.95	-3.37
Cr+COOH2	-3.91	-5.03	-3.57	-4.71
Cr+COOH3	-3.31	-4.17	-2.93	-3.82
Cr+COOH4	-6.38	-7.13	-5.93	-6.71
Cr+COOH0	-1.57	-1.25	-0.99	-0.67

Further evaluation of the various mechanisms considered for the removal of chromium using the acid function, it was observed that CrCOOH0 (physisorption) exhibited the least exergonicity (ΔGads = -0.67 eV), whereas CrCOOH4 displayed the highest exergonicity (ΔGads = -6.71 eV). These results suggest that the removal of chromium via the acid function is more favourable in water through a single-bond molecular interaction of Cr-C. The lower exergonicity observed in the case of the acid function, indicating a weaker interaction, can be attributed to the presence of the O-H bond, which likely reduces the polarity of the carboxylic acid, dipole moment, and consequently, the adsorption strength, as supported by the literature (Qianqian et al., 2022).

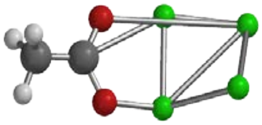
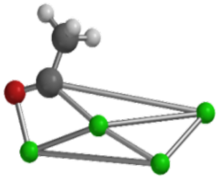
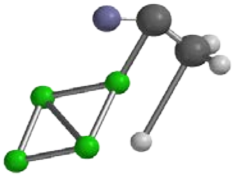
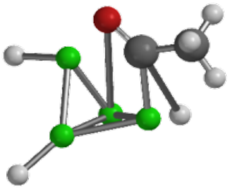
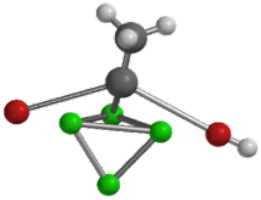
3.4 Summary of The Most Stable Adsorption Mechanism Across Different Functions

Table 10 summarizes the findings regarding the most stable adsorption mechanisms for attracting chromium (Cr) metal on surfaces based on aldehyde (-CHO), carbonyl (-CO), nitrile (-CN), carboxylate (-COO), alcohol (-COH), and carboxylic acid (-COOH) functional groups. The table presents their 3D optimized geometrical structures, adsorption strength (Eads), and Gibbs free energy (ΔGads) values obtained for various interaction mechanisms across different functional surface models.

In general, all functional groups were observed to exhibit varying levels of interaction strengths, following this trend: carboxylate (-COO) > carbonyl (-CO) > acid (-COOH) > alcohol (-COH) > aldehyde (-CHO) > nitrile (-CN). Surfaces rich in carboxylate were found to demonstrate the highest interaction strength, while nitrile (-CN) exhibited the least strength, consistent with their relative adsorption trends.

Further assessment of the exergonicity trend for various functional surfaces in Cr removal revealed a pattern consistent with the adsorption strength. Although the ease of the solvation effect favouring the adsorption process followed the reverse order of the reported trend for functional surfaces, confirming the superiority of surfaces with alcohol (-COH), aldehyde (-CHO), and nitrile (-CN).

Table 10. The adsorption strengths and Gibbs free energies for the most stable optimized geometry using solvated energies computed for the use of B3LYP-D3+SOL in our study (Note white is H, grey is C, red is O, green is Cr, and blue is N).

Cr+...	Most Stable Optimized Geometry	Eads (eV)	ΔGads (eV)
-COO2		-13.46	-12.78
-CO4		-10.60	-10.07
-CN3		-3.38	-2.96
-CHO4		-3.99	-3.58
-COH3		-4.92	-4.89
-COOH4		-7.13	-6.71

Considering the interplay of solvation effects, exergonicity, and adsorption strength for the investigated functional surface models (i.e., adsorbent functional fragments), it is suggested that surfaces rich in carboxylate (-COO) and/or carbonyl (-CO) functions would best facilitate chromium metal removal based on the results obtained in this study. Additionally, the study further demonstrates that nitrile (-CN) has the least effect on adsorption strength for chromium metal due to its lowest adsorption strength and least exergonicity, as indicated by its lower Eads and ΔGads. These findings align with existing literature (Touihri et al., 2021) that experimentally investigated chromium metal removal through the adsorption process, highlighting the significant influence of carboxylate and carbonyl functions on the adsorption activity.

Other research studies that support similar findings include Gunatilake (2016), which demonstrates a significant difference in peak intensity for carboxylate (1610-1550 cm-1) on both rice husk and sawdust, without a significant peak for the carbonyl (2100-1800 cm-1) function on either material in the Cr (III) removal process. Atieh et al. (2010) similarly confirmed that functionalizing carbon nanotubes with carboxylic acid to obtain its functional derivatives, like carboxylate on the material surface, significantly improves its Cr (III) removal level or concentration.

However, it is also important to note that the analysis of existing experimental reports in the literature shows that the significance of carboxylate to chromium removal is not limited to Cr(III) only but also extends to Cr(VI). This was confirmed in the report by Yu and Liao (2023), which shows that the change in carboxylate (around 1630, i.e., 1750-1500 cm-1) absorption intensity confirms their participation and influences on the adsorption strength, as indicated by the changes observed in its peaks on FTIR spectra.

4. CONCLUSIONS AND RECOMMENDATIONS

In response to the escalating environmental threats posed by the discharge of toxic materials, this study delved into the intricate realm of removing heavy metals, particularly chromium, from industrial effluents. Our investigation, employing B3LYP-D3 dispersion-corrected density functional theory (DFT) calculations, meticulously explored the influence of various functional groups on the adsorption process in the aqueous form. The diverse models with peculiar functional groups, including carboxylate, carbonyl, nitrile, aldehyde, alcohol, and carboxylic acid, were systematically scrutinized for their interactions with chromium.

Carboxylate groups, commonly found in acidic treatments and carbonyl groups, were identified as highly effective and reactive in chromium removal, exhibiting strong adsorption strengths and exergonic interactions, even in the presence of solvent(water). The study emphasized the potential of carboxylate and carbonyl-rich sorbents (or substances) in the adsorption of chromium from industrial effluents. Unlike, the other groups like nitrile and alcohol functions that showed a lower potential or feasibility for chromium removal, due to the weaker adsorption energy and lesser exergonic interactions obtained for the function.

In summary, this study emphasizes the critical role of functional groups in designing treatment processes for chromium-containing industrial effluents. It highlights the effectiveness of specific functional groups, such as carboxylate and carbonyl, in removing chromium, thereby supporting sustainable and environmentally friendly water treatment practices. Sorbents designed with a significant presence of these functional groups show promise in adsorbing pollutants like chromium from untreated industrial effluents, which are often discharged into water bodies, posing risks to aquatic life and the quality of water in rural communities.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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