



LIGAND ASSISTED ADSORPTION OF Cr(VI) IONS FROM AQUEOUS SAMPLES USING NANO-ADSORBENTS

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Abstract

The present study explores the utilization of naturally available organic acid-infused nano-adsorbents as effective ligands for the adsorption of Cr(VI) ions from aqueous samples. The nanomaterials were infused with natural organic acids using the solvent dispersion procedure. These infused organic acids play a crucial role in facilitating ligational interactions between metal ions and adsorbent particles. After the adsorption of Cr(VI) ions from 250 ppm aqueous dichromate solution the isolated adsorbent was leached with 2% nitric acid and assessed for Chromium content using Atomic absorption spectroscopy (AAS). Similarly, the regenerative efficacy of adsorbents was evaluated under thermal and electrolytic conditions using AAS. The ligational interactions of organic acids with metal ions and adsorbents was determined using Mass spectrometry. Among the natural acid ligands investigated, L-Glutamic acid demonstrated a notable increase in adsorption efficiency, reaching up to 33.5% when compared to non-infused control nano-adsorbents. This novel ligand-assisted adsorption strategy proves effective not only in adsorption but also in regenerating the adsorbents under thermal and electrolytic induction. L-Glutamic acid was found to be the most efficient facilitating agent for regenerative adsorbent design with Graphene-oxide which exhibited 20.1% Desorption rate which is approximately 5 times more than that of undoped Graphene-oxide, where as its efficiency further increased under electrolytic desorption with 21.3% of regeneration. The mass spectral analysis supports the metal-ligand interactions, particularly the prominent peak at m/z: 270.02, highlighting the robust Cr-L-Glutamic acid interactions over Graphene-oxide. The present study underscores the promising candidature of novel adsorbent systems by conglomerating Nano-adsorbents with natural organic acid ligands for prominent adsorption efficacy with substantial regeneration of adsorbent especially using Graphene-oxide-L-Glutamic acid system which offers promising avenues for the development of sustainable and effective remediation strategies for contaminated environments.

Keywords: Adsorption, Ligands, Desorption, Nano-adsorbents.

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1. Introduction

Cr(VI) ions are well-known human carcinogens primarily associated with lung and respiratory organ malignancies which emerged as a prominent concern as they degrade slowly and can linger in soil and water for long periods due to their strong environmental persistence^[1,2]. Their extended presence in the environment raises the possibility of organism exposure and possible bioaccumulation in food systems. Cr(VI) ions are actively involved in cell-propagative physiology which leads to DNA mutation and causes cellular damage, which may result in cancer and other genetic disorders^[3]. Cr(VI) pollution of soil and groundwater is mostly caused by industrial processes such as wood preservation, leather tanning, and chrome plating^[4]. Its existence in the environment can also be attributed to natural processes like rock weathering and volcanic eruptions^[5].

It is imperative to eliminate chromium residues from water bodies to safeguard public health, maintain environmental integrity, and guarantee adherence to safety and regulatory requirements. The efficacy of these Nano-adsorbents can be greatly enhanced by ligand doping^[6]. When the ligands combine with Cr(VI) ions to produce stable complexes that are easier for the nano adsorbents to adsorb onto their surface^[7]. These properties provide the Cr(VI)-ligand complexes with more binding sites, increasing their adsorption capability of Ligand assisted adsorption process. The adsorption of Cr(VI) presents a significant challenge owing to its potent oxidizing nature, complicating its removal from aqueous solutions. To overcome this hurdle, researchers have explored the stabilization of Cr(VI) utilizing specific multi-composite mixed nanoparticles. However, the synthesis of these nanoparticles proves to be non-feasible or unstable, posing a limitation in their practical application for efficient Cr(VI) adsorption^[8]. This challenge underscores the need for further research to develop robust synthesis methods or alternative approaches to stabilize Cr(VI) adsorbents, thereby enhancing their efficacy in environmental remediation efforts. In addition to this, the regeneration of nano-adsorbents proves challenging due to the development of irreversible direct chemical interactions between metal ions and nanoparticles. While regeneration is essential for sustainable use, it is hindered by these interactions, limiting the effectiveness of traditional methods. However, advancements in structural modifications of nanomaterials through tailored synthetic routes offer promise in enhancing regeneration capabilities. Despite the potential benefits, these

modifications are often deemed non-feasible and costly, highlighting the need for further research into cost-effective and practical approaches to address the regeneration challenges of nano-adsorbents^[9].

The present study focused on the comprehensive investigation into the adsorption studies of Cr(VI) ions from aqueous solutions using ligand-assisted adsorption. Through a systematic experimental approach, encompassing different naturally available carboxylic acid ligands and varying experimental conditions, we explore the efficiency of ligand-assisted adsorption in adsorbing Cr(VI) species. In this research, we have designed and developed a novel approach for Ligand-assisted Cr(VI) ion adsorption and Desorption strategies. Usually, adsorbents get saturated with metal ions over time, reducing their effectiveness. Desorption helps regenerate the adsorbent, making it available for reuse^[10]. Moreover, desorption enables the recovery of metal ions, reducing the need for constant replacement of adsorbents. This can be cost-effective in large-scale water treatment processes^[11]. Recent research suggests that desorption contributes to the development of advanced adsorbent materials with enhanced desorption properties, leading to more efficient water treatment processes^[12]. In the present study, the desorption process was carried out under thermal and electrolytic conditions for an effective understanding of adsorbate-adsorbent linkages.

2. Materials and Methods

Nano-adsorbents (Graphene-oxide, NP-SiO₂, Nano-Montmorillonite clay) were first impregnated with naturally occurring organic acids (L-Glutamic acid, citric acid, stearic acid, and nicotinic acid) by dissolving them in an appropriate solvent and stirred for 10 min and kept under the probe sonicator for 6 h. The solvent was then evaporated, leaving the organic acids adhered to the nano-adsorbent surface. These activated nano-adsorbents were then employed in batch adsorption experiments, where they were added to the aqueous solution of dichromate ions. The mixture was agitated for 24 h time and filtered. These filtered Nano-adsorbents were tested for Chromium content using AAS analysis.

2.1. Metal ion Adsorption Studies

Potassium dichromate was dissolved in analytical grade double distilled water to make up 250 ppm (concerning elemental Chromium) solution. 1 gm of adsorbent material was infused with 0.10 g of naturally occurring organic acids separately by dissolving the acids in 10 mL of suitable solvents (Ethyl acetate for Stearic acid; Hot Water for

Glutamic acid; Water for Citric acid; Ethanol for Nicotinic acid) and stirred this solution with the adsorbent and kept under the probe sonicator (Labman Automatic PRO 250) with frequency tuned @ 20 KHz for 6 hours. To the acid-infused-adsorbent 50mL of 250ppm metal solution was added and kept for mechanical stirring for 1 hour and kept at room temperature for 24 hours. The adsorbents were filtered off and washed with distilled water for 3 times and dried in hot air oven for 12 hours at 60°C. The adsorbent then leached with 2% HNO₃ and adsorbed metal content was estimated using Atomic Absorption Spectroscopy (AAS) in Thermo-Scientific iCE 3000 series Equipment.

2.2. Metal ion Desorption Studies

To study the thermal desorption process 1.0 g of pre-adsorbed adsorbent sample was taken in 250mL beaker with 200 mL of Analytical grade distilled water and kept under the thermostatic chamber (TMAX-80F) at 95°C for 1 hour. After that, the adsorbent was filtered off and dried in the hot-air oven at the regulated temperature of 60°C for 1hr. The sample was then analyzed for Chromium content using AAS. Whereas, for the electrolytic-induced Desorption process 1.0 g of pre-adsorbed adsorbent sample was taken in 250mL beaker with 200 mL of Analytical grade distilled water and kept under the thermostatic chamber (TMAX-80F) at 25°C and inserted two platinum electrodes which were connected to a DC-battery with 3.0 V potential difference for about 6 hr. The adsorbent sample was then filtered and dried in the hot-air oven at a regulated temperature of 60°C for 1hr. The sample was analyzed for Chromium content using AAS.

3. Results and Discussion

3.1. Metal adsorption studies

Adsorption of Cr(VI) on different adsorbent systems exhibited clear variations when evaluated by AAS which reflects the dissimilitude in chemical and physical interactions between adsorbent sites and adsorbate moieties. Ligand-assisted activation of adsorbents provide transparent elevation in adsorbability in most of cases depending on the chemical and structural affinities. Infusion of nicotinic acid into nano-adsorbents leads to an increase in adsorption efficacy ranging from 2.3% to 18.8%, demonstrating its effectiveness [Table 1], [Figure 1]. The highest adsorption capacity was achieved with the Montmorillonite nano clay-nicotinic acid system, resulting in a remarkable increase of 186.36 ppm of Cr(VI) adsorption. Similarly, infusion with citric acid enhances adsorption quantities by 0.3% to 11.2%, with the Montmorillonite-citric acid combination exhibiting the highest increase of 111.06 ppm compared to undoped montmorillonite nano-clay. Notably, infusion of nano-adsorbents with L-glutamic acid yields exceptional results, enhancing adsorption by 5.0% to 33.5% compared to control nano-adsorbents. The most significant increase in adsorption was observed in the graphene-oxide-L-glutamic acid adsorbent system, with a notable increase of 373.6 ppm. These findings underscore the effectiveness of doping nano-adsorbents with select acids to enhance their adsorption capabilities, offering promising avenues for advanced environmental remediation strategies.

Table 1. Adsorption of Cr(VI) on various pre-designed Nano-adsorbent systems.

Nano-Adsorbent System	Adsorption of Cr(VI) in ppm
Nano-Montmorillonite Clay (50-100nm)	990.03±0.50
SiO ₂ -NP(50-100)	907.4±5.71
Graphene-oxide (3-6 nm)	1115.26±2.45
Nano Montmorillonite Clay-Stearic Acid	988.46±2.91
Nano Montmorillonite Clay-Citric Acid	1101.1±1.01
Nano Montmorillonite Clay-Nicotinic Acid	1176.4±3.74
Nano Montmorillonite Clay-L-Glutamic Acid	1235.36±1.02
SiO ₂ NP-Stearic Acid	902.26±1.15
SiO ₂ NP-Citric Acid	910.76±0.45
SiO ₂ NP-Nicotinic Acid	928.83±1.00
SiO ₂ NP-L-Glutamic Acid	953.36±1.10
Graphene-Oxide-Stearic Acid	1101.43±1.10
Graphene-Oxide-Citric Acid	1136.4±1.21
Graphene-Oxide-Nicotinic Acid	1143.53±2.12
Graphene-Oxide-L-Glutamic Acid	1488.97±1.00

Figure 1. Adsorption pattern of Cr(VI) on various pre-activated Nano-adsorbents.

3.2. Metal Desorption Studies

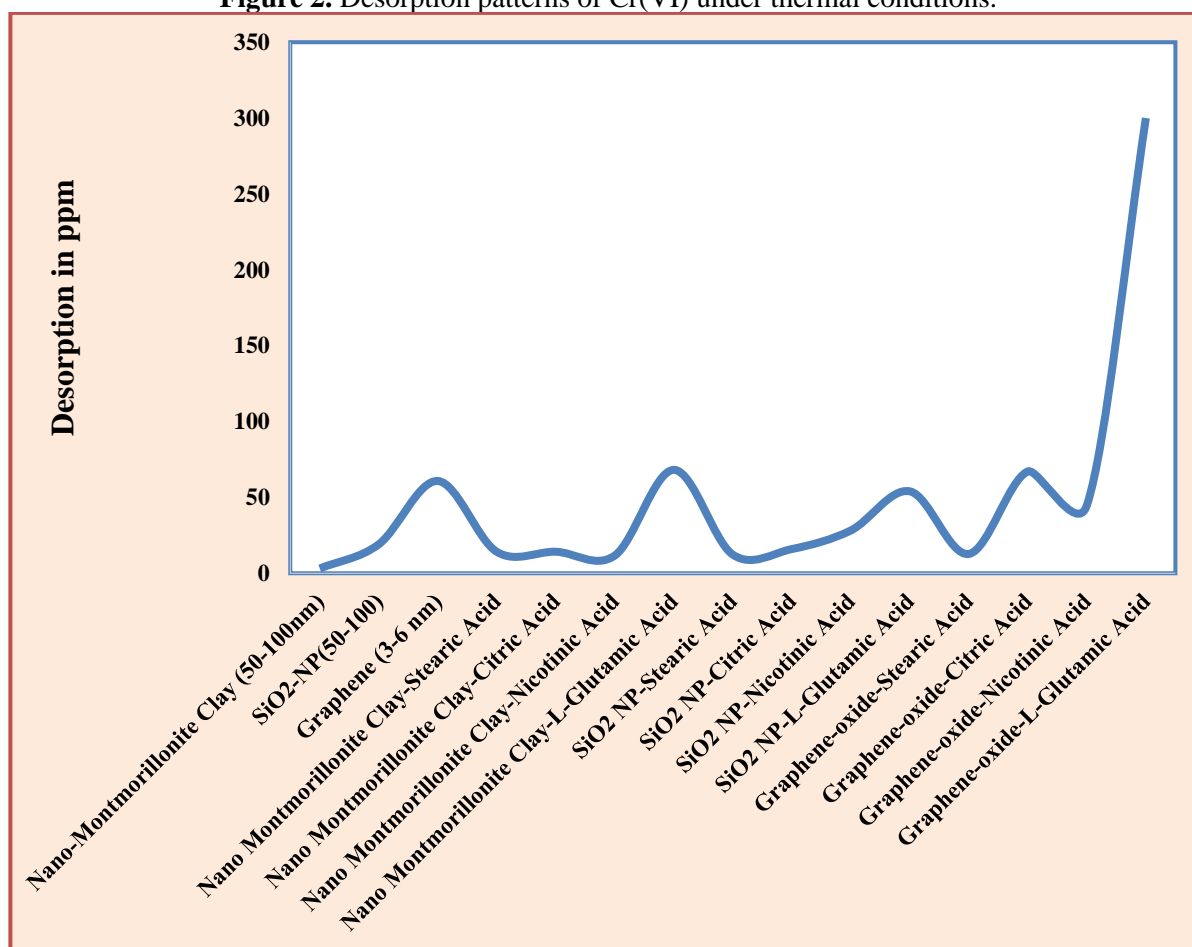
3.2.1. Thermal desorption studies

Thermal-induced desorption involves raising the temperature of the adsorbent-metal ion complex, which increases the kinetic energy of the system. The increased energy facilitates the breaking of metal-adsorbent bonds, leading to the release of metal ions into the solution^[13]. The results indicate notable variations in the desorption capacities among the different adsorbent systems [Table 2]. The significantly higher desorption concentration observed for Graphene-Oxide-L-Glutamic Acid (300.06 ppm) suggests a reversible bonding interaction for Cr(VI) ions with infused ligands in this particular system. The infusion of naturally

occurring organic acids into nano-adsorbents significantly enhances the thermal desorption of Cr(VI), thereby improving the regenerative properties of the adsorbent material. Among the various organic acids studied, L-glutamic acid emerged as the most potent enhancer of desorption, particularly when combined with graphene oxide, resulting in a remarkable 20.1% increase in desorption rate compared to undoped graphene oxide. It is evident from the present study that doping of L-Glutamic acid on Graphene-Oxide induces its reversibility of the adsorption process under thermal treatment by 4.9 times when compared with the control Graphene-Oxide adsorbent.

Table 2. Thermal Desorption of Cr(VI) from various pre-designed Nano-adsorbent systems.

Nano Adsorbent System	Adsorption of Cr(VI) in ppm after Thermal Treatment in aqueous Conditions	Desorption in ppm
Nano-Montmorillonite Clay (50-100nm)	987.36±0.83	3.13
SiO ₂ -NP(50-100)	891.8±0.65	19.10
Graphene-Oxide (3-6 nm)	1056.96±1.00	60.83
Nano Montmorillonite Clay-Stearic Acid	971.06±0.90	14.13
Nano Montmorillonite Clay-Citric Acid	1088.00±0.95	14.20
Nano Montmorillonite Clay-Nicotinic Acid	1166.50±1.21	11.70
Nano Montmorillonite Clay-L-Glutamic Acid	1167.20±1.12	68.16
SiO ₂ NP-Stearic Acid	891.23±1.40	12.26
SiO ₂ NP-Citric Acid	895.23±0.41	15.96
SiO ₂ NP-Nicotinic Acid	901.56±0.61	28.23
SiO ₂ NP-L-Glutamic Acid	899.36±1.61	54.00
Graphene-Oxide-Stearic Acid	1088.16±0.83	12.73
Graphene-Oxide-Citric Acid	1070.66±0.55	67.13
Graphene-Oxide-Nicotinic Acid	1101.06±0.72	44.83
Graphene-Oxide-L-Glutamic Acid	1188.9±0.91	300.06

Figure 2. Desorption patterns of Cr(VI) under thermal conditions.

3.2.2. Electrolytic Induced Desorption Studies

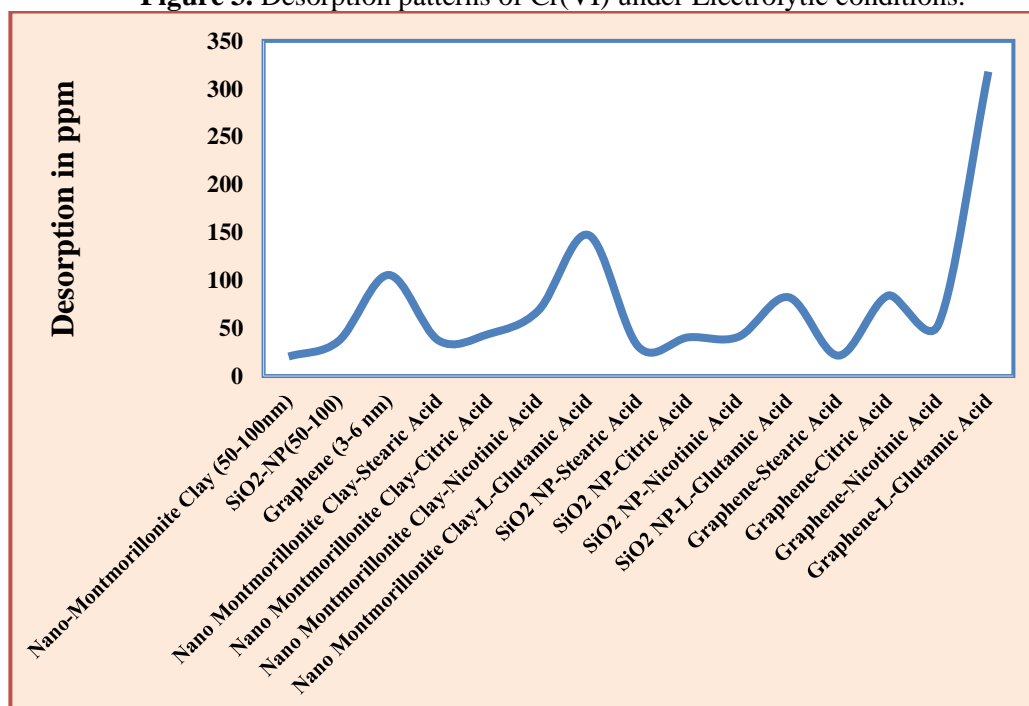
The application of an electric field can increase the mobility of metal ions in solution, reducing their affinity for the adsorbent surface and facilitating desorption^[14] but the Electrolytic induction allows for selective desorption of specific metal ions based on their electrochemical properties, providing a controlled and targeted approach. Electrolytic desorption proved to be a more

effective regeneration method compared to thermal desorption, demonstrating an increase in desorption ranging from 8.0 ppm to 58.6 ppm [Table 3], [Figure 3]. The Graphene-oxide-L-glutamic acid system exhibited the highest regenerative property, achieving a desorption rate of 317.8 ppm, representing a substantial increase of 21.3% over baseline.

Table 3. Electrolytic desorption patterns of Cr(VI) from pre-activated Nano-adsorbents.

Nano Adsorbent System	Adsorption of Cr(VI) in ppm after Electrolytic induction in aqueous Conditions	Desorption in ppm
Nano-Montmorillonite Clay (50-100nm)	969.7±0.87	20.33
SiO ₂ -NP(50-100)	870.83±0.94	36.56
Graphene-Oxide (3-6 nm)	1009.73±0.97	105.53
Nano Montmorillonite Clay-Stearic Acid	951.30±1.05	37.16
Nano Montmorillonite Clay-Citric Acid	1057.26±0.47	43.83
Nano Montmorillonite Clay-Nicotinic Acid	1107.86±1.20	68.53
Nano Montmorillonite Clay-L-Glutamic Acid	1088.10±0.91	147.26
SiO ₂ NP-Stearic Acid	871.70±0.60	30.56
SiO ₂ NP-Citric Acid	870.30±0.52	40.46
SiO ₂ NP-Nicotinic Acid	887.83±0.92	41.00
SiO ₂ NP-L-Glutamic Acid	871.06±0.90	82.30
Graphene-Oxide-Stearic Acid	1080.10±0.91	21.33
Graphene-Oxide-Citric Acid	1052.30±0.52	84.10
Graphene-Oxide-Nicotinic Acid	1089.60±0.36	53.93
Graphene-Oxide-L-Glutamic Acid	1171.10±0.95	317.87

Figure 3. Desorption patterns of Cr(VI) under Electrolytic conditions.

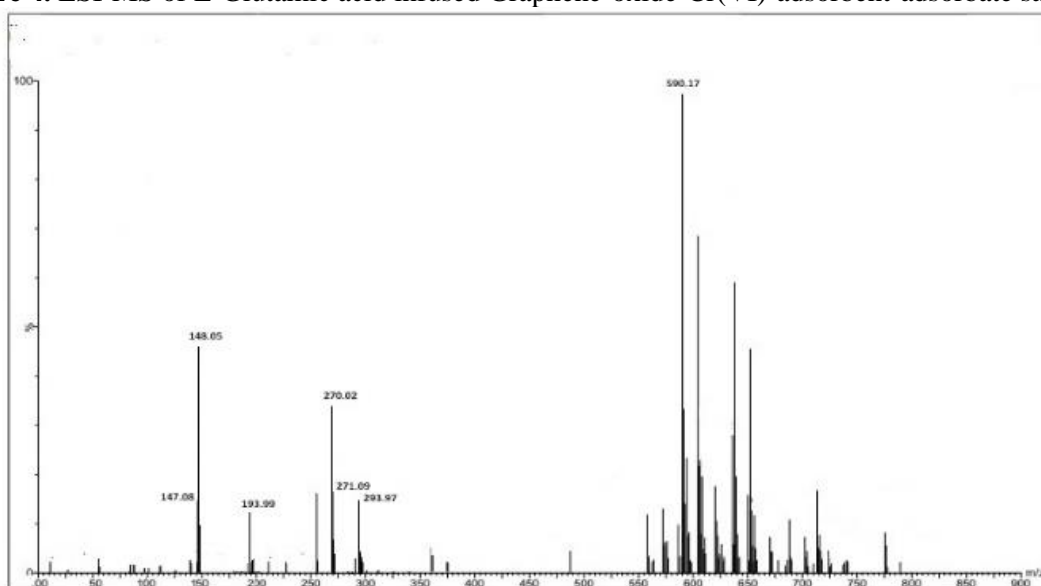


3.3. Mass Spectrometric Analysis

The MS-ESI spectrum of Cr(VI) ion adsorbed Graphene-Oxide-L-Glutamic acid sample showed various peaks corresponding to Graphene-Oxide in the range of m/z 550 to 750 [Figure 4]. The base peak is recorded at m/z : 590.17 with 100% intensity. Apart from these, certain peaks which are specific to M-L interactions suggest that the chemical interactions between L-Glutamic acid and Cr(VI). The peak at m/z : 270.02 (M+1) plausibly corresponds to $[\text{Cr}(\text{C}_5\text{H}_7\text{NO}_4)(\text{H}_2\text{O})_4]^+$ complex which indicates bidentate ligational bonding between Cr(III) and L-Glutamate. The dichromate ion in aqueous condition interacts with L-Glutamic acid and is reduced to Cr(III) which

further reacts with Glutamate to form above said complex. Owing to the oxidizing property of dichromate L-Glutamic acid oxidized into keto acid ($\text{C}_5\text{H}_6\text{O}_5$) which is identified with the help of the peaks at m/z : 147.08(M+1), 148.05(M+2). The peak corresponding to potassium dichromate recorded at m/z : 293.97 suggests metal adsorption without ligand interface i.e. dichromate ion directly involved chemical interactions with graphene-Oxide layers due to its high polarity. Similarly, potassium chromate which is formed due to the reduction of dichromate in the aqueous condition found at m/z : 193.99 (M+1) exhibited the direct chemical adsorption of metal ions on the Graphene-Oxide layer.

Figure 4. ESI-MS of L-Glutamic acid infused Graphene-oxide-Cr(VI)-adsorbent-adsorbate sample.



4. Conclusion

Naturally available organic acid-infused Nano-adsorbents provided a prominent route for efficient adsorption of Cr(VI) ions from aqueous samples. The infused organic acids facilitate the ligandic interactions with metal ions and bind them chemically on the surface of Nano-adsorbents which promotes enhanced adsorption. Among the natural acid ligands L-Glutamic acid showed raised adsorption up to 30.5% when compared to non-infused control nano-adsorbents. This novel strategy of ligand-assisted adsorption also provides an effective approach for adsorbent regeneration under thermal and electrolytic induction owing to reversible metal-ligand interaction leading to the desorption of Chromium from adsorbent up to 317.87 ppm. The Mass spectral analysis also substantiates the metal-ligand interactions, especially the peak at m/z : 270.02 strongly abet the Cr-L-Glutamic acid interactions over Graphene-oxide. In conclusion, the outlook of the present

study helps design and develop efficient strategies for the remediation of Cr(VI) contaminants from water samples in the view of human and ecological safeguards.

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6. References

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