Knowledge-based Engineering and Sciences (2023), **4**, (3), 35–50
doi:10.51526/kbes.2023.4.3.35-50

RESEARCH PAPER

Capabilities of Novel Carbon Nano Adsorbents in Evaluating the Extraction of 2-Nitrophenol and Heavy Metal from Aqueous Solutions

Hamza A. Asmaly,[1] Nassereldeen Kabbashi,[1] Ma'an Fahmi Al-Khatib,[1] Md Zahangir Alam,[2] and Mohamed A. Yassin[*,3]

[1]Department of Biotechnology Engineering, International Islamic University Malaysia, Gombak, 53100 Kuala Lumpur, Malaysia
[2]Department of Chemical Engineering and Sustainability, International Islamic University Malaysia, Gombak, 53100 Kuala Lumpur, Malaysia
[3]Interdisciplinary Research Centre for Membranes and Water Security, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[*]Corresponding author. Email: mohamedgadir@kfupm.edu.sa

(Received 08 November 2023; revised 13 December 2023; accepted 24 December 2023; first published online 31 December 2023)

Abstract

This study primarily focused on evaluating the efficacy of Metal Oxide-infused Carbon Nano Adsorbents (CNAs), which included both Carbon Nanotubes and Carbon Nanofibers, in removing Cd^{+2}, Cr^{+3}, and 2-NP from water solutions. We synthesized and analyzed four distinct types of CNAs, each impregnated with either Al_2O_3, TiO_2, Fe_2O_3, or Cu_2O_3. The metal content in these CNAs was determined by comparing their dry and calcined weights. To investigate their properties, we utilized various techniques such as Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Energy-Dispersive Xray Spectroscopy (EDX), and Thermal Gravimetric Analysis (TGA). These methods helped us understand their morphological traits, surface areas, pore structures, metal oxide distributions, and thermal stabilities, thereby confirming their adsorption effectiveness for pollutants. The findings indicated that CNAs altered with metal oxides showed higher surface areas and adsorption abilities than their unmodified counterparts. Specifically, CNAs/TiO_2 exhibited the most significant increase in surface area $\left(140\ m^2/g\right)$ and pore volume $\left(0.460\ cm^3/g\right)$, which resulted in an enhanced adsorption capacity for Cd^{+3} at 11.4(mg/g), surpassing the 9.5(mg/g) capacity of pure CNAs with surface area $\left(90\ m^2/g\right)$, and pore volume $\left(0.331\ cm^3/g\right)$. Similarly, CNAs/$Al_2O_3$ demonstrated an increased surface area of 100 $\left(\ m^2/g\right)$, surpassing that of pure CNAs. This enhancement led to a significant improvement in adsorption capacities, elevating the uptake for Cr^{+3} from 32.2 to 52 (mg/g) and for 2-NP from 24.8 to 49.6(mg/g). This enhancement in adsorption efficiency is attributed to the increased surface area and improved surface chemistry due to the incorporation of Titania and Alumina, which proved more effective than modifications with copper oxide and Ferric oxide. These insights emphasize the significance of selecting appropriate metal oxides for modifying CNAs, as this can greatly impact their ability to target various contaminants, thus contributing to the development of more advanced water purification methods using CNAs/MO.

Keywords: Nitrophenols; Chromium; Cadmium; Carbon Nano Adsorbents; Adsorption.

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1. Introduction

The contamination of water resources with hazardous substances like Cadmium (Cd), Chromium (Cr), and Nitrophenols (NPs), particularly 2-Nitrophenol (2-NP), poses significant environmental and health risks. These contaminants, originating from various industrial activities such as battery production, electroplating, smelting, and the improper disposal of electronic waste, have been found to seep into groundwater and surface water systems. Despite existing methods like bioremediation, chemical oxidation, and adsorption, there remain significant challenges in effectively removing these pollutants from water. Traditional carbon-based adsorbents, such as Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs), while promising, have shown limitations in their adsorption capacity and efficiency, particularly when dealing with a range of contaminants. This is largely due to their restricted surface area, pore size, and limited interaction with certain pollutant molecules. Therefore, there is an urgent need for more effective, efficient, and versatile adsorbent materials capable of addressing the broad spectrum of contaminants found in water.

Cadmium, a hazardous heavy metal, poses significant health risks and is commonly used in various industrial processes such as battery production, electroplating, and smelting. It can be released into the environment through activities like mining, waste incineration, and improper disposal of electronic devices. Human actions like industrial discharge, waste disposal, and agricultural practices can also lead to cadmium contamination in groundwater, making it one of the most concerning water pollutants [1]. The United Nations' health agency had defined an upper allowable limit of 0.003 mg/L pertaining to cadmium in potable water to address these hazards [2].

Chromium, an essential industrial metal known for its durability, is released into the environment by processes like tanning and electroplating, posing threats to water sources [3], [4]. The WHO has set a safe limit of 0.05 mg/L for chromium in drinking water [5]. Nitrophenols (NPs), common but toxic compounds, are priority contaminants according to the USEPA [6]; [7]-[9], and their presence in water sources can have serious health implications [10]. Effective removal methods for 2-Nitrophenols include bioremediation, chemical oxidation, photocatalysis, adsorption, magnetic separation, and reverse osmosis, addressing their potential health risks when present in water sources [11]-[16]. Adsorption, a well-studied method, is considered highly effective and economically viable for removing various organic contaminants from water. Researchers have faced challenges in eliminating heavy metal ions from wastewater [17]-[25]. CNTs, known for cleanliness, porosity, functional surfaces, size, site density, and structural form, are highlighted for their effectiveness in adsorbing heavy metal ions in water solutions [26]-[28]. Impregnating metals onto carbon nanomaterials is an effective water treatment method, as previous research has shown. It improves the performance of carbon nanotubes (CNTs) in removing heavy metals from water. During calcination, metal oxides are crucial in enhancing adsorption capacity. Studies confirm the effectiveness of modifying CNTs with metal oxides, like magnesium oxide and iron oxide, to eliminate various contaminants from water [29]-[34]. In our previous research, limitations were observed in the effectiveness of carbon nanofibers (CNFs) in eliminating certain contaminants due to their limited surface area and pore space [35]. Furthermore, the use of CNFs in research is limited due to their low interaction with other functional groups, leading to a reduction in their ability to adsorb. Nonetheless, these limitations of CNFs can be overcome by combining them with MCNTs, which have a high ability to interact with other functional groups like Metal oxides. For instance, metal impregnation has been shown to significantly enhance the performance of carbon nanotubes (CNTs), as it forms metal oxide groups on their surfaces, leading to superior adsorption capacities compared to unmodified CNTs. Through the fusion of carbon nanofibers (CNFs) and CNTs, and their subsequent modification, we can fabricate hybrid adsorbent materials (CNAs/MO). These materials exhibit amplified properties and are apt for various water purification applications.

The primary gap in the previous work lies in the limited efficiency of conventional carbon nanomaterials in adsorbing a range of pollutants. This study aims to address this gap by exploring the potential of hybrid adsorbent materials, specifically a combination of Conical Carbon Nanofiber (CCNF) and Multi-walled Carbon Nanotube (MCNT), infused with various metal oxides. The motivation behind this research is to enhance the adsorption capacity of carbon nanomaterials and expand their applicability in water treatment, particularly for contaminants like Cr, Cd, and 2-NP.

This study is driven by the hypothesis that the surface modification of CNAs with metal oxides through wet impregnation techniques can significantly improve their adsorptive performance. The innovative approach of combining CCNF and MCNT aims to leverage the synergistic properties of these nanomaterials, thereby addressing the limitations of conventional adsorbents. The research is further motivated by the need for more effective, cost-efficient, and sustainable solutions for water purification, aligning with global environmental protection and public health objectives.

The goal of this research is to evaluate the efficacy of a hybrid adsorbent material (CNA/MO), comprising Conical Carbon Nanofiber (CCNF) and Multi-walled Carbon Nanotube (MCNT), in removing Cr, Cd, and 2-NP from water. Various metal oxides were used to modify the adsorbent surface through the wet impregnation technique, aiming to identify the most favorable modified adsorbent with Elevated adsorption capability and compare it to the unmodified adsorbent (CNAs). this research seeks to contribute significantly to the field of environmental science and water purification technologies.

This research is significant as it aims to address the critical gap in current water purification methods by developing an innovative hybrid adsorbent material, combining Conical Carbon Nanofiber (CCNF) and Multi-walled Carbon Nanotube (MCNT), infused with various metal oxides. The significance of this research lies in its potential to enhance adsorption efficiency, offer a versatile solution, contribute to public health and environmental protection, align with global standards, and advance water treatment technologies.

2. Meterials and methods

2.1 Materials and Chemicals

The Conical Carbon Nanofibers (CCNFs) utilized in this study were provided by Hebei Liche Zhuoge Environmental Technology Co., Ltd. This selection was based on their prior application in my earlier study [37] and their use in other research works [38]-[40]. They had a purity of 99.99% and sizes that span from 75 to 25 nm across, and from 20 to 30 um in length. The Nanotube Carbon with Multiple Walls (MWCNTs) used in the experiment were obtained from Sigma Aldrich and had a trace metal content of less than 2000ppm. The MWCNTs had an average diameter of 8.7 nm, outer diameter of 6.0 nm, length varying from 2.5 to 20µ, inner diameter of 2.0 nm, and a purity of 98.99%. All the chemicals employed lin the study were of analytical grade, including Ferric Nitrate $Fe\,(NO_3)_3 \cdot 9H_2O$, Copper (II) acetate monohydrate $Cu\,(OOCCH_3)_2 \cdot H_2O$ with a purity of 98%, Aluminum Nitrate nonahydrate ($Al\,(NO_3)_3 \cdot 9H_2O$) with a purity of 98%, Titanium Nitrate $Ti\,(NO_3)_4$ with a purity of 97%, 2-Nitrophenol $C_6H_5NO_3$ in powder form, Chromium Nitrate anhydrous $Cr\,(NO_3)_3$ with a purity of 98.5%, Cadmium Nitrate tetrahydrate $Cd\,(NO_3)_2 \cdot 4H_2O$ with a purity of 98.5%, Sodium Hydroxide (NaOH), Nitric acid (HNO_3), Acetone (C_3H_6O) with a purity of 98%, and Ethanol with a purity of less than 98%.

2.2 Synthesis of Carbon Nano Adsorbent / Metal oxides (CNAs/MO) nanocomposites

2.2.1 Collection and Refinement of the CNMs

The method followed in this process aligns with the techniques used in my earlier studies [41]-[43] and their use in other research works [44], [45]. In this approach, 5 grams of Conical Carbon Nanofibers (CCNFs) and an equal amount of Multi-Walled Carbon Nanotubes (MCNTs) were separately placed into two 500 ml beakers. The materials underwent an acid treatment with 35% hydrochloric acid to purify them. After the acid treatment, filtration and rinsing with deionized water were carried out until the runoff water reached a neutral pH, indicating successful removal of excess acid and contaminants. The solutions were then agitated for one hour using a magnetic stirrer to ensure uniform mixing. Subsequently, the mixtures were dried under vacuum conditions at a constant 40°C temperature. The dried samples were combined in a 600ml centrifuge tube and thoroughly blended using a high-speed vortex machine for two hours. This rigorous procedure aimed to create a well-mixed, highly homogeneous carbon nano adsorbent composite. The resulting dried CNAs were set aside as the primary material for further experiments, particularly for synthesizing modified CNAs integrated with metal oxides, ensuring the integrity and consistency of the nanomaterials for subsequent studies. (See Appendix -A1) illustrates the detailed procedure for each nano carbon material.

2.2.2 Synthesis of the CNAs/TiO_2, CNAs/Fe_2O_3, CNAs/Al_2O_3andCNAs/Cu_2O_3 nanocomposites

Exceeding a 20% metal loading on Carbon Nanotubes (CNTs) in earlier studies led to issues such as metal particle aggregation, which compromised structural integrity, weakened mechanical strength, and reduced lifespan. Metal overloading also masked a significant portion of the CNMs' surface, hindering their primary adsorption capabilities. To mitigate these concerns, it's advisable to adhere to the 20 % limit for metal loading in CNAs total composition. Following this recommendation, the procedure for synthesizing the CNAs/Al_2O_3 nanocomposite commenced with the thorough mixing of 1.0 g of dried CNTs and 1.0g of CNFs in 200 ml round-bottom flasks, forming CNAs (See Appendix -A2). For the impregnation process, distinct chemicals were added to 2 gm of dried CNAs in individual 500 ml beakers as follows: 5.561g of Aluminum Nitrate, 2.473g of Titanium Nitrate, 2.89g of Ferric Nitrate, and 1.257g of Copper Acetate. Each mixture was dissolved in 200ml of 98% ethanol, then sonicated for 2 hours. Afterward, the mixtures were dried at 80°C for 24 hours to eliminate ethanol and moisture. This was followed by calcination at 350°C for 3 hours, ensuring the removal of organic precursors, such as nitrates and acetate groups. This process also facilitated the formation of metal oxides, eradication of possible residues from the impregnation, and improved the adherence of metal oxide nanoparticles (like titanium oxide, aluminum oxide, ferric oxide, and copper oxide) to the CNAs particles' surface. Subsequently, the samples were rinsed using deionized water and dried overnight. Yield calculations were performed to assess the stability and efficiency of the impregnated material by using the equations (for equations refer to Appendix A-1).

2.3 Preparation of the stock solutions

To create a 1000 ppm solution of 2-NP, 1.0g of 2-NP powder was dissolved in 1000 ml of deionized water. Similarly, a 1000 ppm Cd (II) solution was prepared by dissolving 2.744 g of Cadmium nitrate Tetrahydrate in 1000ml of purified water, and a 1000 ppm Cr (III) solution was created by dissolving 4.578 g of Chromium Nitrate anhydrate in 1000ml of deionized water. These solutions were then serially diluted to produce a stock solution with an initial concentration of 50 ppm. To ensure thorough mixing and pH control, a magnetic stirrer was used, and nitric acid (HNO3) and sodium hydroxide (NaOH) were added to the solutions. Buffer solutions were also employed to maintain a stable pH level during the preparation process.

2.4 Batch adsorption studies

The efficiency of CNAs/MO in adsorbing 2-NP, Cr, and Cd was assessed through batch adsorption studies at room temperature. An orbital shaker (Max Q430 Hp) from Thermo Scientific was used to achieve the desired agitation speed (See Appendix -A3). The test parameters included a 20-hour contact time, an agitation speed of 250 rpm, a solution pH of 6.5, an adsorbent dose of 20 mg, and an initial concentration of 50 mg/L. Final concentrations of 2-NP, Cr, and Cd were measured in 100 ml volumetric flasks. To ensure accuracy, all glassware underwent an acid wash using 5% nitric acid, and ultra-pure water was used to prevent metal ions from adhering to the flask's sides. 2-NP concentration was determined by measuring the maximum absorbance wavelength at 317 nm with a

UV-visible spectrophotometer (Shimadzu - Japan), while Cd and Cr concentrations were identified using an Atomic Spectrometer Analyzer (Perkin Elmer). Adsorption capacities for 2-NP, Cr, and Cd were calculated using Equation (3) (for equations refer to Appendix A-2).

2.5 Characterization Techniques

The crystallinity of metallic composite adsorbents (CNA/MO) was assessed through X-ray diffraction (XRD) analysis using a Rigaku diffractometer (Miniflex II) with specific parameters. High-Resolution Electron Scanning Microscope (SEM) examination followed after coating the samples with gold using a Quorum instrument (Q150TE). Energy dispersive X-ray spectroscopy (EDX) was employed for elemental analysis. Surface area was determined by nitrogen adsorption/desorption isotherms at 77.35 K using a Micromeritics automated gas sorption system (ASAP2020). Samples were degassed before testing, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation [36]. The stability of synthesized CNAs impregnated with metal oxides was assessed with a TGA 4000 (PerkinElmer) to ensure their suitability for subsequent adsorption tests conducted with a mechanical shaker.

3. Result and Discussion

3.1 Evaluation of the Impregnation Process

The impregnation rate can be finely tuned to achieve desired characteristics or improve the efficiency of the Carbon Nano-Additives (CNAs). Generally, increasing the impregnation rate results in a higher deposition of the introduced material, enhancing its effectiveness. However, this increase might also impact other aspects such as pore structure, surface area, and durability. Based on the equations (1), (2), and (3) (Appendix A-1). Table S-B1 in Appendix A-3, provides details of the experimental impregnation process, including the dry yield, calcined yield, and the specific impregnation achieved in this CNAs/Metal Oxide experiment. The result plotted in Fig 1 shows that the highest impregnation yield was observed with Aluminum oxide at 68 %, followed by titanium oxide at around 67%. Impregnation yields for Ferric oxide and Copper oxide were commendable at approximately 47% and 40%, respectively. Variations in impregnation percentages can be attributed to factors such as incomplete conversion of metal salts to their elemental state and the washing process after impregnation. Washing removed free Fe and Cu ions to a greater extent, resulting in reduced final metal content, while minimal Ti and Al were removed during this step.

Table 1: *Analysis of the surface area and pore dimensions for the unaltered and chemically modified CNAs/MO.*

Sr	Adsorbent	S_{BET} (m^2/g)	Langmuir Surface Area (cm^3/g)	Pore volume (cm^3/g)	Pore size (nm)	Nanoparticle Size (nm)
1	Pure CNAs	90.4025	135.2402	0.331271	14.34033	129.8666
2	CNAs/ Al_2O_3	100.4681	138.1723	0.176357	7.02142	119.4409
3	CNAs / TiO_2	139.8597	204.6875	0.460247	13.16310	85.8003
4	CNAs / Fe_2O_3	109.7521	161.2355	0.296420	10.80326	109.3373
5	CNAs / Cu_2O_3	92.9651	134.4168	0.306373	13.62186	133.3851

3.2 Adsorbents Characterization

3.2.1 BET Surface Area Analysis

Surface area plays a crucial role in the adsorption of pollutants in water and evaluating the impact of metal oxide impregnation on the surface area of Carbon Nano Adsorbents (CNAs) is essential.

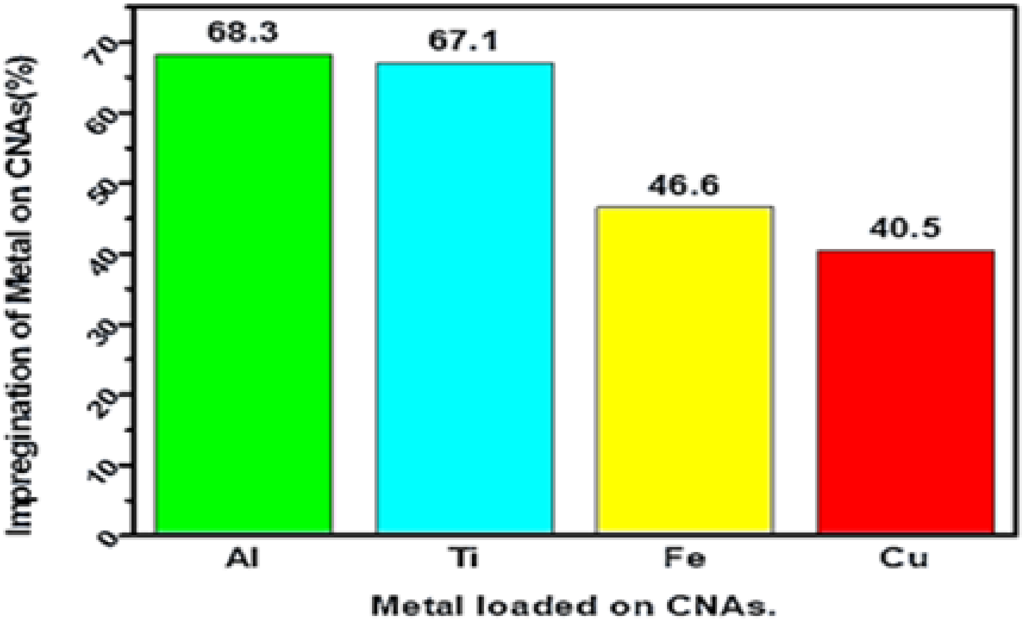

Figure 1: *Appraisal of the Impregnation of Metals on the CNAs.*

Nitrogen adsorption/desorption isotherms were measured at 77°C using a gas sorption system. Specific surface area (S_{BET}) was calculated using the BET and Langmuir equations. Fig 2 and table 1 depict the adsorption and desorption processes for all CNAs modified with metal oxides. The surface areas of Pure CNAs, CNAs/ Al_2O_3, CNAs/Fe_2O_3, and CNAs/TiO_2 nanocomposites were found to be 90, 100, 109, and 140 m^2/g, respectively. This increase in surface area in the modified samples suggests that integrating Al_2O_3, Fe_2O_3, and TiO_2 metals with CNAs creates new attributes on the CNA's surface, expanding its overall effective surface area. These additional metal surfaces provide more sites for chemical interactions and absorption processes, enhancing the overall surface area. However, the surface area of CNAs/Cu_2O_3 remained at 92 m/g, which is not significantly different from the 90 m^2/g observed in pure CNAs. This indicates that the copper oxide primarily affected the external surface of CNAs without significantly altering their internal structure, resulting in minimal changes to the surface area.

3.2.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was conducted to assess the homogeneity and thermal stability of the CNA/MO nanocomposites as shown in Fig 3(a). Approximately 5mg of each adsorbent was analyzed under nitrogen gas. CNAs/Al_2O_3 and CNAs/TiO_2 exhibited high thermal stability, remaining stable up to 648°C and 567°C, respectively. They experienced a single stage of decomposition, fully decomposing at around 970°C for CNAs/Al_2O_3 and just over 998°C for CNAs/TiO_2. In contrast, unmodified CNAs displayed decent stability up to 550°C and fully decomposed at 900°C. CNAs modified with Titanium oxide and Aluminum oxide demonstrated superior stability compared to pure CNAs. CNAs/ Cu_2O_3 and CNAs/Fe_2O_3 also underwent singlestage decomposition, but at lower temperatures compared to CNAs/Al_2O_3 and CNAs/TiO_2. CNAs/Fe_2O_3 and CNAs/Cu_2O_3 maintained good stability up to approximately 450°C and 460°C, respectively. TGA analysis reveals that CNAs enhanced with TiO_2 and Al_2O_3 exhibit superior thermal stability compared to pure CNAs. This improved stability, crucial in high-temperature settings, affects both the structure and adsorption effectiveness of carbon nanotubes and nanofibers in CNAs. It ensures the preservation of active sites and surface area, essential for adsorption, while preventing structural changes. Conversely, CNAs modified with Fe_2O_3 and Cu_2O_3 show similar stability to unmodified CNAs, highlighting the significant impact of metal oxide selection on their thermal and structural properties and subsequent adsorption capabilities.

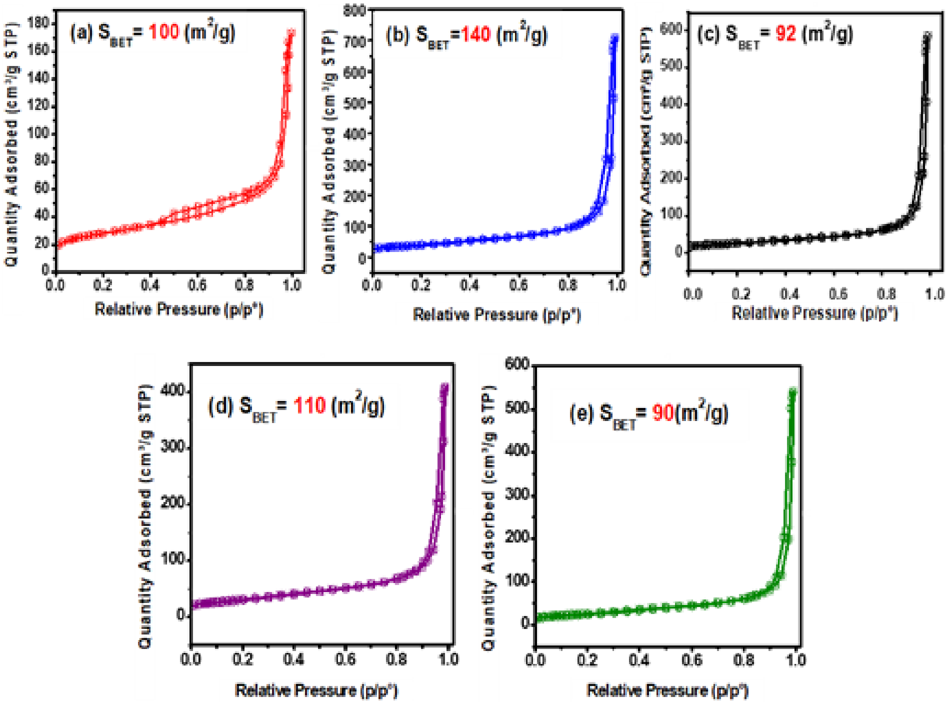

Figure 2: *Surface area measurements of (a)* CNAs/Al_2O_3 *(b)* CNAs/TiO_2 *(c)* CNAs/Cu_2O_3 *(d)* CNAs/Fe_2O_3 *(e) Pure* CNAs

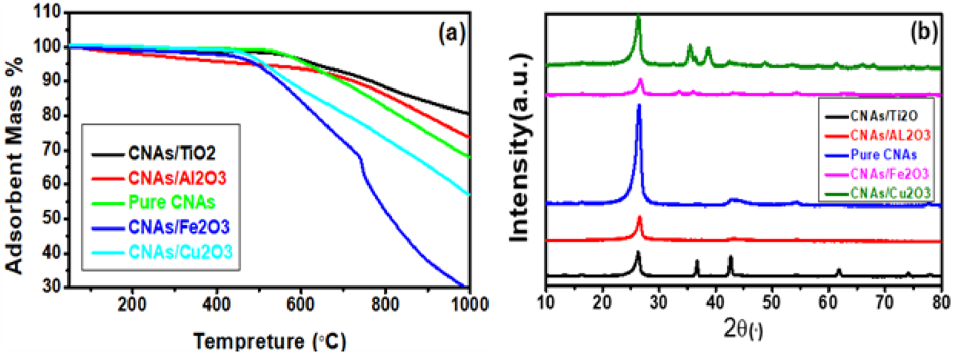

Figure 3: *(a) TGA measurements of the Pure and Modified CNAs, (b) XRD profiles of the unmodified CNAs and those modified with metal oxides.*

3.2.3 X-Ray Diffraction (XRD) of CNA/MO

An extensive analysis was conducted on the crystal and carbonaceous structures of a Carbon NanoAdditives (CNAs) blend concerning their interaction with various metallic oxides, specifically Alumina, Copper Oxide, Titania, and Ferric oxide. X-ray diffraction (XRD) was employed, and the results are depicted in Fig 3 (b). Pure CNAs, without any metallic oxide, exhibited a single peak at approximately $\sim 25.6°$, corresponding to the (002) crystallographic planes of hexagonal graphite crystals. In contrast, multiple peaks at various positions were observed in the other modified samples. In each modified sample, a significant peak at around 26.5° indicated the presence of C (002) crystallographic planes of hexagonal graphite crystals. CNAs/Al_2O_3 displayed additional peaks at $\sim 33.5°$, $\sim 36.3°$, and $\sim 54.5°$, signifying the presence of Al_2O_3. CNAs/Tir O exhibited five distinct peaks, with two major ones at $\sim 36.7°$ and $\sim 42.7°$, and three smaller ones around $\sim 61.8°$, $\sim 73.7°$, and $\sim 77.6°$, indicating the presence of Titanium Oxide. For CNAs/Fe_2O_3, four minor peaks at $\sim 33.5°$, $\sim 35.9°$, and $\sim 54.4°$ suggested effective linking of Fe_2O_3 particles with pure CNAs. CNAs /Al_2O_3 showed two notable peaks at $\sim 35.6°$ and 38.9°, along with several smaller peaks at $\sim 61.4°$ and $\sim 68.3°$, validating effective interaction between CNAs and CNAs/Al_2O_3 particles. The crystallinity differences highlighted in Fig 3(b) reveal that Pure CNAs and those modified with copper oxide and Ferric oxide possess a higher degree of crystallinity compared to CNAs altered with Titania and Alumina. This pronounced crystallinity, especially in Pure CNAs and CNAs/Cu_2O_3, suggests a more ordered structure, potentially reducing pore variety and surface area, as confirmed by BET analysis shown in Fig 2(c) and (e). This structural aspect could adversely impact the adsorption efficiency for 2-NP, Cr, and Cd, indicated in Fig 6, by limiting binding sites and slowing down adsorption kinetics due to uniform pore structures. In contrast, CNAs modified with Titania and Alumina display a more amorphous structure, leading to increased porosity and surface area, as evidenced by the BET analysis. This structural variation enhances their adsorption capabilities for all pollutants (2-NP, Cr, and Cd), as demonstrated in Fig 6. The broader range of pore sizes and greater surface areas, as shown in Fig 2(a) and (b), improve adsorption capacity and kinetics, facilitating the diffusion of 2-NP, Cr, and Cd molecules through their pores.

3.2.4 Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS)

The Scanning Electron Microscope (SEM) images in Figure 4 illustrate the presence of Fe_2O_3 in the CNAs' components. The images reveal diverse morphologies at both micro and nano scales on the CNAs' surface after modification with Ferric oxide. Notably, carbon nanotubes, carbon fibers, and Ferric oxide particles are distinctly visible. On the nano adsorbent surfaces, Fe_2O_3 nanoparticles appear as black crystal structures of Fe_2O_3 with a small average size, distributed widely across the surfaces of carbon nanotubes and forming small crystal particles with varying diameters. Additionally, random clusters or groupings of Fe_2O_3 metal oxide can be observed on the surface. In the high-resolution image, the layered structure of CNTs and CNFs is clearly visible, marked by white lines, indicating potential interactions or bonding between these carbon materials and Ferric oxide, which could influence the CNAs' performance properties.

To verify the incorporation of metal oxides on the surfaces of the CNAs, Energy Dispersive Spectroscopy (EDS) was employed. The EDS method was instrumental in determining the elemental composition of CNAs combined with Al_2O_3, TiO_2, Fe_2O_3, and Cu_2O_3, and confirming the presence of metal oxide nanoparticles on the CNAs. The outcomes derived from the EDX analysis corroborate the findings presented by the SEM imagery in Figure 5. This consistency between the two methods strengthens the validity of the observed results and provides a more comprehensive understanding of the type of synthesized adsorbents. A comprehensive summary of the EDS analysis is provided in Appendix B2. An interesting observation was that all samples had varying levels of oxygen content, attributed to the metal oxides containing oxygen on the CNAs surfaces. Appendix B2 lists the proportional mass of the individual elements. Notably, in the spectrum, the peaks of titanium, iron, copper, and aluminum are clearly discernible (see Appendix B2).

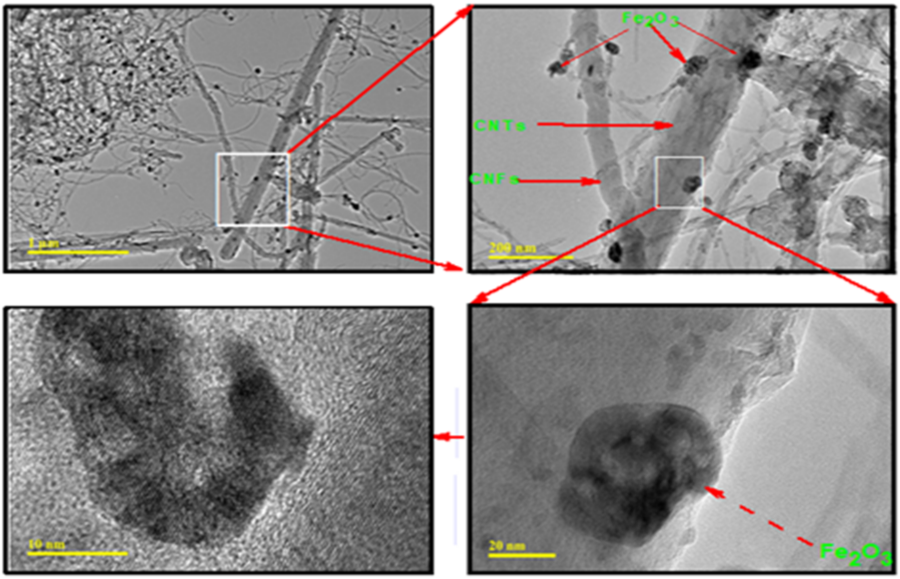

Figure 4: *Reflective FE-SEM visuals of the Speckled CNAs integrated with Ferric oxide.*

3.3 Adsorption of 2-Nitrophenol, Chromium and Cadmium

The study aimed to assess the effectiveness of four different CNAs/MO types in removing 2-NP, Cr^{+3} and Cd^{+2} from solution. Tests were conducted using 100ml of a solution with a high initial 2-NP, Cr^{+3} and Cd^{+2} concentration of 50ppm. Each test involved introducing an adsorption dose of 20mg and was conducted at room temperature. Before the adsorption experiments, the absorbance of the initial $2-NP, Cr^{+3}$ and Cd^{+2} samples at 50ppm were measured, serving as baseline readings, which were recorded in (see Appendix B3 (a, b, and c)). After exposure to the adsorbents, the remaining $2-NP, Cr^{+3}$ and Cd^{+2} concentrations in the solutions were determined. These equilibrium values provided insights into the efficiency of each absorbent. The data obtained was then used to calculate the Adsorption Capacity for each tested material using equation (4) in Appendix A-2. These calculated values, representing the performance metrics of each CNAs/MO type, were systematically documented in (see Appendix B3). This structured approach offers comprehensive insights into the removal capabilities of each absorbent. The result as shown in Fig 6 (a) the CNAs/MO nanocomposites display superior adsorption capacities when compared to untreated CNAs. Remarkably, CNAs/ AL_2O_3 and CNAs/Ti_2O_3 show pronounced adsorption for 2-NP removal, at about 50 and 36mg/g, respectively. Compared to the capacity of Pure CNAs at (24.8) mg/g, the recorded capacity of CNAs/Al_2O_3 has almost doubled, reaching 50(mg/g), while the CNAs/Ti_2O_3 's has risen by 40%. CNAs /Cu_2O_3 and CNAs/Fe_2O_3 also record improvements, at 34.4% and 5% respectively. Our prior study [35] suggested that processes like acid treatment amplify interactions between adsorbate particles and the nanocomposite surfaces. This interaction intensification, coupled with the added presence of the MO, considerably bolsters the CNAs' adsorptive properties. Turning to Fig 6(b), CNAs/MO nanocomposites demonstrate a more efficient adsorption capability than their unmodified counterparts, especially in Cr^{3+} ion removal. Among them, CNAs/Ti_2O_3 stands out with an impressive capability of roughly 52mg/g, emphasizing its proficiency in Cr^{3+} ion capture. When juxtaposed with the Pure CNAs, CNAs/AL_2O_3 sees a performance spike of about

61%. Meanwhile, can /Cu_2O_3 acanCNA /Fe_2O_3 exhibit in Fig 6(c) suggests that CNAs/MO nanocomposites outshine the Pure CNAs in adsorption capacities. In the context of Cd^{2+} removal, CNAs/AL_2O_3 and CNAs/Ti_2O_3 both all manifest marginally higher capabilities, registering at 11.10 and 11.40mg/g, respectively. When set against their unmodified version, CNAs/AL_2O_3 and CNAs/Ti_2O_3 report increments of roughly 16% and 20%, respectively, with CNAs/Cu_2O_3 and CNAs/Fe_2O_3 both around 13%. In general, these four metal-infused CNAs seem more adept at $2-$NP and Cr^{+3} recovery than at cadmium removal. This variance likely stems from the metals on CNAs creating more resilient chemical interactions with and 2-NP might also sway their respective affinities with CANs/MO surfaces, resulting in differing adsorption efficacies.

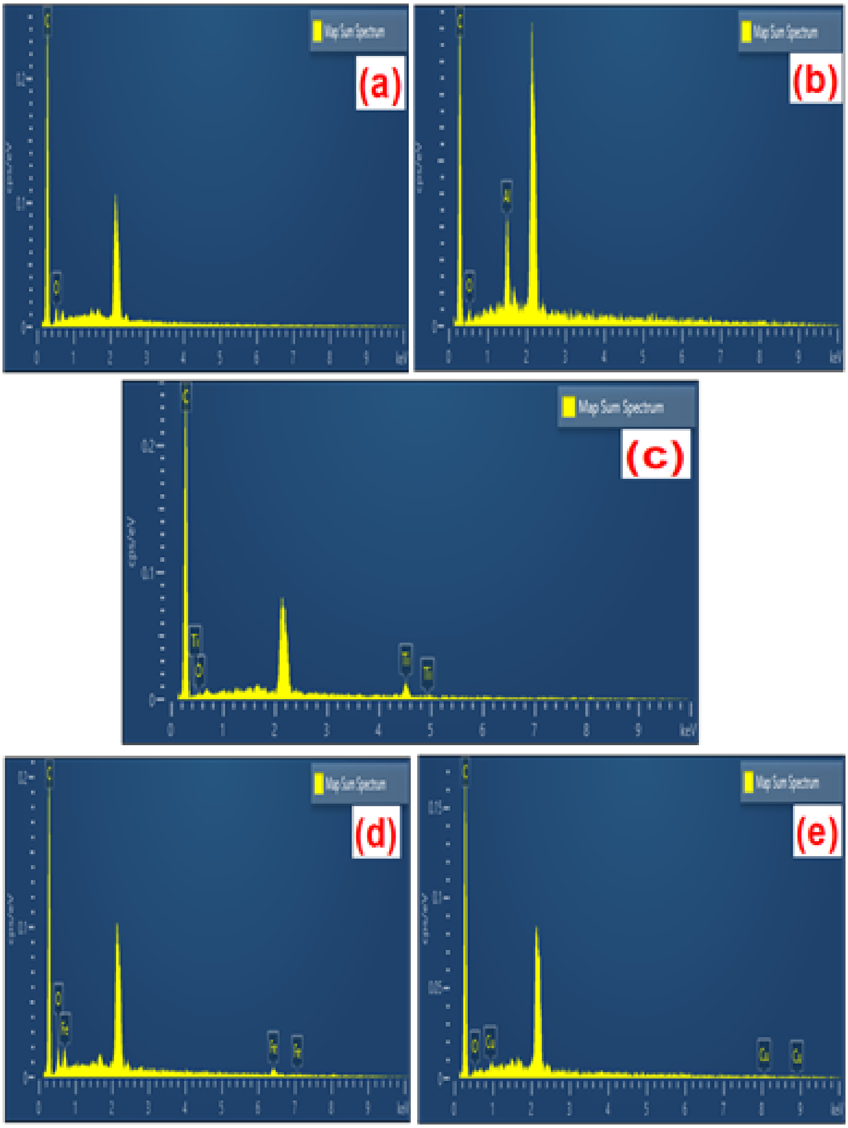

Figure 5: *EDX Spectrums of the (a) Pure CNAs and (b)* CANs/AL_2O_3 *(C)* CNAs/TiO_2 *(d)* CNAs/Fe_2O_3 *(e) CNAs* /Cu_2O_3

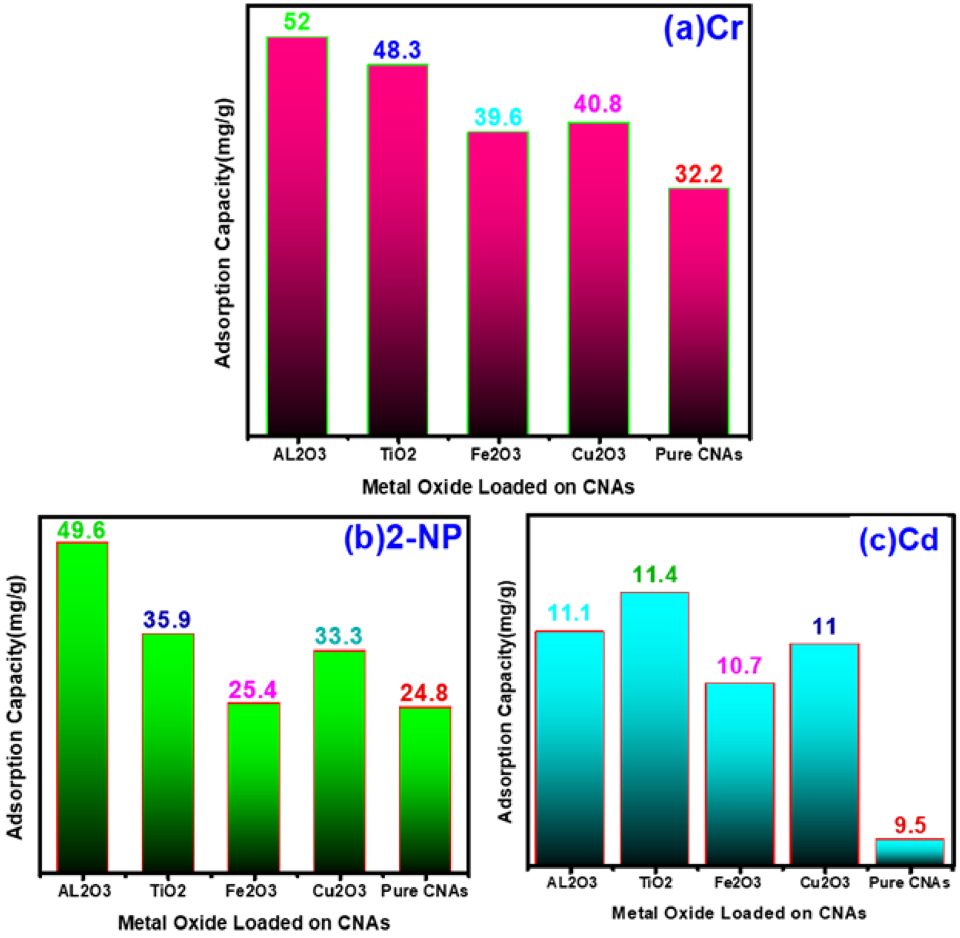

Figure 6: *The absorption Potential of the CNA/MO for recovering 2-NP,* Cr^{+3} *and* Cd^{+2}.

3.3.1 Evaluating CNAs' Adsorption Capabilities for Chromium, Cadmium, and 2-NP

Figure 7 provides a clear demonstration of the remarkable impact that Titanium oxide and Aluminum oxide have when integrated with Carbon Nano-Additives (CNAs) in the adsorption of pollutants such as 2-nitrophenol (2-NP), Chromium (Cr), and Cadmium (Cd) from water-based solutions. These metal oxides significantly boost the CNAs' adsorption efficiency, outshining the effects imparted by Ferric and Copper oxides. In particular, the combination of CNAs with Aluminum oxide emerges as exceptionally proficient in removing 2-NP and Cr from aqueous environments, achieving results that are unmatched by other combinations. Conversely, when it comes to the extraction of Cadmium, CNAs that are fused with Titanium oxide demonstrate significant performance due to their robust adsorption properties. This highlights the critical role that Titanium oxide plays in enhancing the CNAs' ability to adsorb Cd. As we delve deeper into the performance of various modified adsorbents presented in this study, it becomes evident that CNAs/Al_2O_3 and CNAs/TiO_2 are at the forefront. The distinct composition of these materials leads to a significant improvement in their capacity to adsorb specific contaminants, particularly Cd^{2+}, Cr^{3+}, and 2-NP, when compared to other modified CNAs. This enhancement is vividly captured in Fig 7, which showcases the superior capabilities of both CNAs/Al_2O_3 and CNAs/TiO_2. With such striking outcomes, these two variants firmly establish themselves as top-tier adsorbents in their category. The expertise of CNAs /Al_2O_3 and CNAs/TiO_2 extends beyond the realm of heavy metal adsorption; they are also adept at eliminating organic pollutants from aquatic environments. This versatility positions these CNAs as comprehensive solutions, adeptly engineered to tackle a wide range of pollutants. Their unique chemical structures not only enhance their adsorption capacity but also set new standards in the field of pollutant removal. The prowess of these CNAs is further emphasized when their performance metrics are juxtaposed with those of their peers, solidifying their standing as exceptional adsorbents. The study's findings underscore the unparalleled nature of CNAs/Al_2O_3 and CNAs/TiO_2 in the adsorbent domain. Their distinct chemical composition imbues them with an increased potential for adsorption, thereby elevating them to a benchmarksetting status. This is particularly significant in the context of environmental remediation, where the effective removal of pollutants from water is crucial. The ability of CNAs/Al_2O_3 and CNAs/TiO_2 to outperform other modified CNAs in adsorption efficiency is a testament to their superior design and the effectiveness of their metal oxide enhancements. Moreover, the choice of metal oxide for impregnation plays a pivotal role in determining the overall effectiveness of the CNAs. This study exemplifies how the integration of specific metal oxides, like Titanium oxide and Aluminum oxide, can lead to a profound improvement in the adsorption capacity of CNAs. The tailored approach in selecting these oxides for CNAs modification shows that strategic material design can lead to optimized performance in environmental applications, especially in water purification.

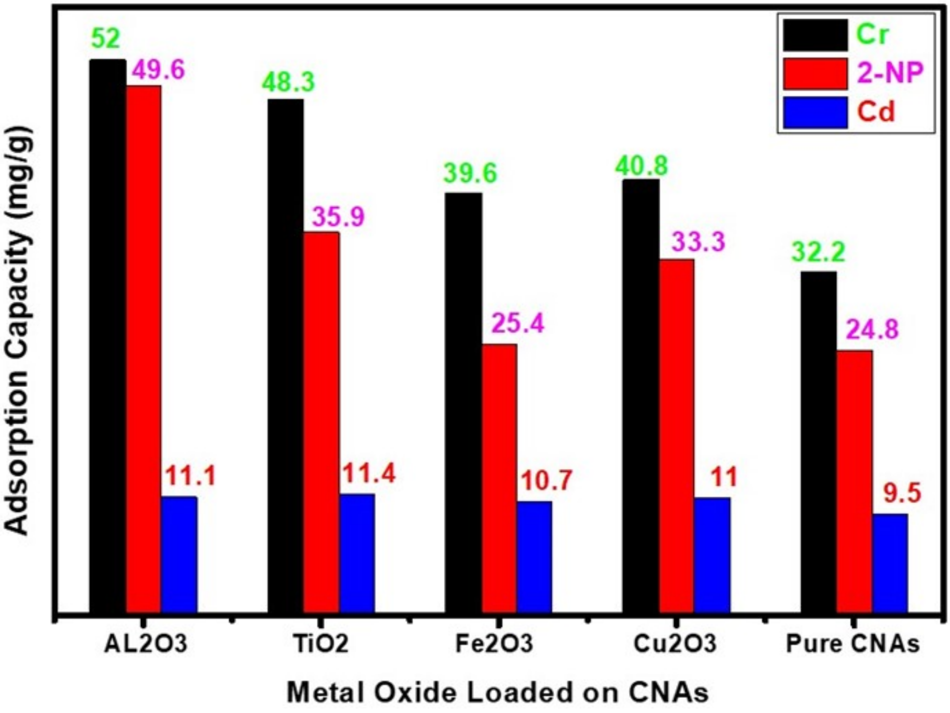

Figure 7: *Comparison between the Adsorptive Abilities of CNAs/MO and the Notable Enhancement in Adsorption Efficiency of CNAs infused with Metal oxides.*

In essence, CNAs/Al_2O_3 and CNAs/TiO_2 emerge not just as mere adsorbents, but as sophisticated solutions for the complex challenge of pollutant removal from aqueous environments. Their efficiency in adsorbing a diverse array of contaminants, coupled with their enhanced chemical and physical properties, marks a significant advancement in the field of adsorption technology. This study's insights into the superior adsorption capabilities of CNAs/Al_2O_3 and CNAs/TiO_2 pave the way for future developments in creating more effective and versatile adsorbents, with the potential to revolutionize water treatment processes and environmental cleanup efforts.

4. Conclusion

The study distinctly highlights the advanced adsorption capabilities of both pure and metal oxideintegrated CNTs/CNFs in extracting Cr, Cd, and 2-NP from water-based mediums. The findings clearly elevate the performance of CNAs/MO nanocomposites when compared to their raw counterparts. Among the tested varieties, CNAs/TiO_2 and CNAs/Al_2O_3 emerge prominently for their exceptional ability to remove a mix of heavy metals and organic compounds. In particular, CNAs/Cu_2O_3 surpasses CNAs/Al_2O_3 in cadmium removal, while CNAs/Fe_2O_3 and CNAs/Al_2O_3 maintain a similar effectiveness. XRD results confirm that the original crystalline and carbondriven architecture of CNAs stays preserved, even with metal oxide additions. Thermal gravimetric analysis affirms the enduring thermal resilience of these adsorbents throughout the adsorption phase. Insights from the BET analysis indicate that metal impregnation can potentially augment, or at the very least, not diminish the surface area of these adsorbents. Furthermore, EDX scrutiny solidly validates the integration of metal oxides within each synthesized sample. Finally, this hybrid Carbon Nano Adsorbent with specific metal oxide exhibits remarkable effectiveness in eliminating a broad spectrum of organic and inorganic contaminants from water. The study conclusively demonstrates that the infusion of specific metal oxides into CNAs significantly enhances their adsorption capabilities for certain pollutants. Al_2O_3 and TiO_2, in particular, showed remarkable improvements in adsorption efficiency for 2-NP and Cr^{3+}, respectively. These findings are critical for advancing water purification strategies, as they suggest that customizing CNAs with appropriate metal oxides can optimize their performance for specific contaminants. The results also underscore the importance of understanding the interactions between metal oxides and carbon nanostructures to develop more effective adsorbent materials for environmental remediation applications. This research doesn't just illuminate the variances in performance across different CNA configurations but also sets the groundwork for designing high-performing adsorption mechanisms by judiciously choosing metal oxides tailored to specific contaminants.

Acknowledgement: The authors would like to convey their heartfelt thanks to the Centre for Membranes and Water Security Center at KFUPM (Saudi Arabia) for their support of characterizing the Nano Carbon composite adsorbents.

Conflicts of Interest: The authors declare no conflict of interest.

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