

Article

Manihot esculenta Leaves Extract Mediated Silver–Clay Nanocomposite for the Adsorption of Cadmium(II) and Chromium(VI) Ions from Aqueous Media

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Abstract

The increasing prevalence of heavy metal contamination in aqueous environments poses severe risks to both human health and the ecosystem. To address this environmental concern, this study focused on the utilization of a nature-based silver clay nanocomposite (NAGC) for the removal of cadmium (Cd(II)) and chromium (Cr(VI)) ions from aqueous media. The NAGC was synthesized through the reduction of silver ions in a clay matrix by employing the leaf of *Manihot esculenta* extract as the reducing agent. The NAGC was characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), Brunauer, Emmett, and Teller (BET) surface area as well as energy-dispersive X-ray spectroscopy (EDX). The adsorption behavior of the NAGC in batch experiments under varying pH, contact time, initial concentration, and adsorbent dosage were investigated for the removal of cadmium and chromium from aqueous media. The optimum adsorption of cadmium ions was 157.87 mg/g, achieved at an initial concentration of 20 mg/L at 1 g dosage at pH 7 for 60 min, while that of chromium was 137.91 mg/g at a metal concentration of 20 mg/L at 1 g dosage at pH 7 for 60 min. The Freundlich isotherm model adequately explained the adsorption data of both Cd(II) and Cr(VI). However, the pseudo-first order (PFO) adequately interpreted the kinetic data for both Cd(II) and Cr(VI).

Keywords: biosynthesis; silver-clay; adsorption; cadmium(II) ions; chromium(VI) ions



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1. Introduction

The presence and persistence of heavy metals in aquatic environments is a serious environmental issue that poses a threat to both human health and aquatic life [1,2]. Cadmium (Cd), a toxic metal, is one of the most hazardous pollutants that can accumulate in aquatic systems, leading to serious health issues such as kidney damage and cancer when ingested by humans or animals [2]. Therefore, removing heavy metals from aqueous media has become an urgent environmental concern. Access to safe drinking water remains a critical challenge in many developing regions, including Akwa Ibom State, Nigeria [3].

The presence of lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As) in drinking water has significant health implications, including neurotoxicity, carcinogenesis, and organ dysfunction. These contaminants often originate from industrial effluents, agricultural runoff, and improper waste disposal practices. Given the economic constraints and limited access to centralized water treatment infrastructure in rural communities, decentralized and cost-effective solutions tailored to local contexts are imperative [4,5].

Nature-based materials such as bricks, asbestos, clay minerals, crock, etc., have gained recognition as viable alternatives for water treatment due to their accessibility, sustainability, and low environmental footprint [6]. Among these, clay minerals exhibit unique adsorption capabilities including high specific surface area, layered structure, and surface charge properties. Montmorillonite, kaolinite, and illite clays are particularly effective as adsorbents due to their cation exchange capacities and ability to immobilize toxic metal ions. Furthermore, silver nanoparticles (AgNPs) have been widely recognized for their antimicrobial and catalytic properties, offering dual functionality in water treatment systems by simultaneously addressing microbial and chemical contamination. The integration of silver nanoparticles into a clay matrix has the potential to create a robust nanocomposite with enhanced adsorption capacity, antimicrobial properties, and chemical stability [7]. This approach leverages the inherent adsorptive properties of clay and the surface reactivity of AgNPs, forming a synergistic system capable of targeting both dissolved metals and pathogens. However, ensuring the biocompatibility and sustainability of such materials is critical. Green synthesis provides an eco-friendly alternative to chemical reduction methods, reducing the environmental and health risks associated with conventional synthesis pathways [8,9].

Manihot esculenta, commonly known as cassava, is a tropical plant characterized by its starchy tubers and distinctively lobed leaves [10]. The leaf extract is rich in phytochemicals, which contribute to its reducing properties [11]. Upon extraction, the aqueous solvent facilitates the solubility of these bioactive compounds, imparting strong electron-donating abilities that enable the reduction of metal ions into their elemental forms. The phenolic constituents in the extract interact with metal ions to form stable complexes, making *Manihot esculenta* leaf extract an effective and eco-friendly bioreducing agent in the synthesis of nanoparticles and environmental remediation processes [12].

Akwa Ibom State is characterized by diverse water sources, including shallow aquifers, streams, and rainwater [13]. Despite their availability, these sources are often susceptible to heavy metal contamination, particularly in regions impacted by oil exploration and artisanal mining activities. Traditional water treatment practices, such as boiling or the use of alum for sedimentation, are inadequate for heavy metal removal [14]. Moreover, high costs and technical complexity limit the deployment of advanced treatment technologies like reverse osmosis and ion exchange in rural settings [15,16]. While existing water treatment methods in Akwa Ibom State may not adequately address the rising contamination levels, particularly from industrial activities, there is limited research on the application of innovative, sustainable nanocomposite materials in local contexts. This study seeks to evaluate the performance, sustainability, and practicality of silver-clay nanocomposites in enhancing water quality, thereby contributing to more effective remediation strategies for safe drinking water in the region.

This study aims to develop and evaluate the efficiency of a NAgC for the removal of cadmium (Cd(II)) and chromium (Cr(VI)) ions from aqueous systems. The NAgC was synthesized through the green reduction of silver ions within a clay matrix using *Manihot esculenta* leaf extract as a bioreducing agent.

2. Materials and Methods

2.1. Chemicals

All chemicals used in this study were of analytical grade and used without further purification. Silver nitrate (AgNO_3 , $\geq 99\%$ purity, CAS: 7761-88-8), hydrochloric acid (HCl , 37 wt.%, CAS: 7647-01-0), sodium hydroxide (NaOH , $\geq 98\%$, CAS: 1310-73-2), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$, CAS: 10022-68-1), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, $\geq 99\%$, CAS: 7778-50-9) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany). Deionized water was used for the preparation of all solutions. Stock solutions of $\text{Cd}(\text{II})$ and $\text{Cr}(\text{VI})$ were prepared by accurately weighing 2.744 g of cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and 2.828 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), respectively, and dissolving each in a small volume of deionized water; the solutions were then quantitatively transferred into separate 1 L volumetric flasks and diluted to the mark with deionized water to obtain homogeneous stock solutions of the desired concentrations. Working solutions were prepared by serial dilution. The pH (pH Sensor InPro 2000i SG/120/9823) (Mettler-Toledo International Inc., Greifensee, Switzerland) of the solutions was adjusted using 0.1 M HCl or 0.1 M NaOH as required.

2.2. Plant Preparation

The aqueous extract of *Manihot esculenta* leaves was prepared by collecting fresh *Manihot esculenta* leaves, thoroughly washed with distilled water. The cleaned, air-dried leaves were ground into a fine powder using a mechanical grinder, IKA MF10 Universal Grinder (IKA-Werke GmbH & Co. KG, Staufen, Germany). A predetermined amount of the powdered leaves was then soaked in distilled water at a 1:10 (w/v) ratio and heated for 10 min at 50°C , and then allowed to stand for 24 h at 27°C , with occasional stirring to enhance the extraction of bioactive compounds [17,18]. After the soaking period, the mixture was filtered first through a muslin cloth and subsequently through Whatman No. 1 filter paper (Cytiva, Marlborough, MA, USA) to obtain a clear aqueous extract. The filtrate was concentrated using a RE-52 series rotary evaporator (Yamato Scientific Co., Ltd., Tokyo, Japan) under reduced pressure until the desired concentration was achieved. Finally, the concentrated extract was stored at 4°C in sterile containers for future use. This method is consistent with established protocols for aqueous plant extraction, which aim to optimize the recovery of bioactive compounds for experimental applications [19–21].

2.3. Clay Sample Collection and Preparation

The process began with the collection of clay samples from Ikot Ebom Itam, Akwa Ibom State (Southern Nigeria), known for its high kaolin content, a crucial component for NAgC synthesis [22]. The collected clay was washed and dried at 29°C for 24 h. Adopting a procedure similar to that of Abubakar and Haque [21], the sieved clay powder was immersed in a hydrochloric acid (HCl) solution for 1 h. After the acid treatment, the clay was washed several times with deionized water [23]. Once the washing process was complete, the purified clay was oven-dried at a temperature of about 80°C for 4 h. A controlled and stable environment (the oven) was utilized to minimize contamination and preserve the desired properties of the clay.

2.4. Biosynthesis of the NAgC

The synthesis of the NAgC using *Manihot esculenta* leaf extract was achieved through an eco-friendly green synthesis method. A 2 M solution of AgNO_3 was prepared and added to 5 g of the treated clay. This mixture was rigorously stirred at 350 rpm for 12 h to enable the Ag^+ ions to penetrate the clay matrix, and subsequently, 50 mL of the plant extract was added. The mixture was left for 48 h for sufficient interaction of the bioactive compound

with the Ag^+ prior to centrifugation. The reduction of Ag^+ to AgNPs was confirmed by a visible color shift from light brown to dark brown, indicating nanoparticle formation, as previously reported [24,25].

2.5. Characterization of the NAgC

The NAgC was characterized using several techniques to assess its morphological, spectroscopic, functional, and compositional properties prior to its application in removing Cd(II) and Cr(VI) ions. The TEM technique on a JEM-2100 TEM (JEOL Ltd., Akishima, Tokyo, Japan) at 80 kV was employed to examine surface morphology and agglomeration, while a SEM (Nova Nano SEM 230, FEI, Hillsboro, OR, USA) microscope equipped with an EDX system (Oxford Instruments NanoAnalysis, High Wycombe, Buckinghamshire, UK) was used at 15 kV to determine elemental composition, following a gold coating for charge mitigation. The phase purity, grain size, and crystallinity were investigated using X-ray diffraction on a Rigaku Miniflex 600 diffractometer (Rigaku Corporation, Akishima, Tokyo, Japan) with Cu-K α radiation at 40 kV and 40 mA, scanning from 10° to 70° at 25 °C. Functional group analysis was conducted with a Shimadzu 4100 spectrometer over a range of 4000 to 500 cm^{-1} in solid-state, employing attenuated total reflectance. Finally, the specific surface area and porosity characteristics were measured using the BET method with a Nova 2000e BET surface area analyzer (Quantachrome Instruments, Boynton Beach, FL, USA), following the pre-drying and degassing of samples before nitrogen adsorption and desorption evaluation at controlled pressures. The Scherrer equation, Equation (1) [23–26], elucidated the crystallite size of the clay and NAgC.

$$\text{CS} = K \lambda / (\beta \cos \theta) \quad (1)$$

where CS, the crystallite size, $\lambda = 1.5406 \times 10^{-10}$, Constant [K] = 0.94, full width at half maximum (FWHM) $[\beta] = \text{FWHM} \times \pi/180$, and θ = Bragg angle.

2.6. Batch Adsorption Studies

A series of adsorption experiments were conducted, utilizing varying concentrations of $\text{Cd}(\text{NO}_3)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ solution and NAgC. Stock solutions of cadmium and chromium were prepared by dissolving appropriate amounts of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$, respectively, in deionized water. All adsorption experiments were conducted using single-metal aqueous systems with a plot between quantity adsorbed (Qty) and the individual parameters. Working solutions with concentrations ranging from 0 to 25 mg L^{-1} were prepared by serial dilution. The pH of the solutions was adjusted within the range of pH 0–9 using 0.1 M HCl or 0.1 M NaOH. Batch adsorption experiments were carried out by adding 1 g NAgC to 100 mL of metal ion solution in conical flasks. The mixtures were agitated using an orbital shaker (Solaris Small Open Air Shaker, Thermo Scientific™ SK2000, Thermo Fisher Scientific, Waltham, MA, USA) at a constant speed of 150 rpm at room temperature (± 25 °C).

The contact time was varied between 0 and 150 min to determine equilibrium conditions. After agitation, the mixture was centrifuged to separate the adsorbent from the solution. The concentrations of Cd(II) and Cr(VI) in the supernatant were then read with an atomic absorption spectrophotometer (AAS) (Agilent Technologies, Santa Clara, CA, US) in triplicate while Equations (2) and (3) was used to calculate the quantity and percentage of Cd(II) and Cr(VI) adsorbed, respectively.

$$Q_e = \frac{(C_0 - C_e)}{W} \times V \quad (2)$$

$$\% \text{adsorbed} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

The initial (C_0) and equilibrium (C_e) concentrations in mg/L, V (volume of the Cd(II) and Cr(VI) ions), solution (L), Q_e = amount of Cd(II) and Cr(VI) ions adsorbed per unit mass of NAgC (mg/g), and w (weight of the NAgC) in (g) are applicable in Equations (2) and (3), as referenced earlier. The kinetic and isotherm models are essential tools for analyzing adsorption processes, offering critical information on the efficiency and energetics of adsorbents.

The Langmuir isotherm model and dimensional constant R_L (Equation (4a,b)), respectively, are particularly effective for systems with uniform adsorption, providing parameters such as the maximum adsorption capacity and the adsorption energy, making it highly suitable for the design and optimization of adsorbent systems [26]. In contrast, the Freundlich model (Equation (5)) excels in describing adsorption in heterogeneous systems, especially at lower concentrations of adsorbate, by emphasizing adsorption intensity and capacity [26]. Collectively, these models help provide insights into effective adsorption technologies.

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \quad (4a)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (4b)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where Q_0 = adsorption capacity and K_L = Langmuir adsorption constant [27]. The dimensionless R_L stands for the degree of favorability: it is unfavorable if $R_L > 1$, linear if $R_L = 1$, and favorable if $0 < R_L < 1$ but irreversible if $R_L = 0$. Also, the Freundlich constant n depicts favorability of the adsorption process ($0 < 1/n < 1$, favorable and $1/n > 0$, unfavorable) and K_f is the adsorption capacity of the adsorbent.

Adsorption kinetics, on the other hand, indicate the dependency of the process on time, and popular models employed include PFO (Equation (6)) and PSO (Equation (7)).

$$\log(Q_e - Q_t) = \log Q_{e,cal} - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e,cal}^2} + \frac{1}{Q_{e,cal}} t \quad (7)$$

The Q_t = amounts of Cd(II) and Cr(VI) ions adsorbed (mg/g) at time t , $Q_{e,cal}$ stands for the calculated (or theoretical) adsorption capacity at equilibrium (mg/g), k_1 = PFO rate constant, and k_2 = the pseudo-second order (PSO) rate constant.

2.7. Regeneration of NAgC Adsorbent

The regeneration and reusability of the NAgC were evaluated using chemical desorption methods following the adsorption of Cd(II) and Cr(VI) ions according to reports in [26,27]. After each adsorption cycle, the 0.1 g of used adsorbent was centrifuged (benchtop centrifuge VL-6B) (Hunan Michael Laboratory Instrument Co., Ltd., Changsha, Hunan, China) at 3500 rpm for 10 min and subjected to 50 mL of different regeneration treatments, namely acid washing, base treatment, and chelating agent desorption. For acid regeneration, the NAgC was treated with a 0.1 M HCl solution under continuous agitation at 200 rpm for 60 min to facilitate the desorption of adsorbed metal ions. In the base regeneration method, 0.1 M NaOH solution was used under similar conditions to neutralize surface interactions and release bound ions, while for chelation-based regeneration, 0.05 M EDTA solution was employed to complex the adsorbed metal ions and enhance desorption efficiency. Following each treatment, the adsorbent was thoroughly washed with deionized water until neutral pH, and then dried at 60 °C before reuse in subsequent adsorption cycles. The regenerated NAgC was reused for multiple adsorption–desorption cycles to evaluate its stability and

efficiency. The regeneration efficiency was assessed by comparing the adsorption capacity of the regenerated adsorbent with that of the fresh material over successive cycles.

3. Results

3.1. Morphological Features and Surface Area of NAgC

SEM was used to carry out the morphological characterization of clay and NAgC, as presented in Figure 1A,B [28]. Comparing the raw clay sample (Figure 1A) to the NAgC (Figure 1B), a noticeable difference was observed in agglomeration. The former exhibited significant agglomeration, while the latter displayed discrete particles with a lower level of aggregation attributed to the effects of the metabolites present in the *M. esculenta* extract, as suggested in previous reports [12,29]. The TEM of NAgC (Figure 1C) revealed a high distribution of the majorly spherical and irregularly shaped NAgC as well as a chain-like configuration with sizes below 100 nm. This high distribution, shape, and size of the well-formed NAgC particles could be due to the stabilization and capping properties of the *M. esculenta* leaf extract [29,30]. The shape of the isotherm in Figure 1D provides insights into the characteristics of the material. The inset shows a strong positive relationship between the relative pressure (P/P_0) and the transformed adsorption parameter $1/[Q(P_0/P-1)]$, with $R^2 = 0.9809$, indicating good agreement with the BET adsorption model. The curve appears to be Type IV based on the IUPAC classification, which is indicative of mesoporous materials. The initial horizontal part of the curve represents monolayer–multilayer adsorption, and the latter part, where the curve rises sharply, indicates capillary condensation within the pores with appreciable surface area ($47.221 \text{ m}^2/\text{g}$), pore diameter ($103.6234 \text{ \AA}$), and pore volume ($0.1383 \text{ cm}^3/\text{g}$).

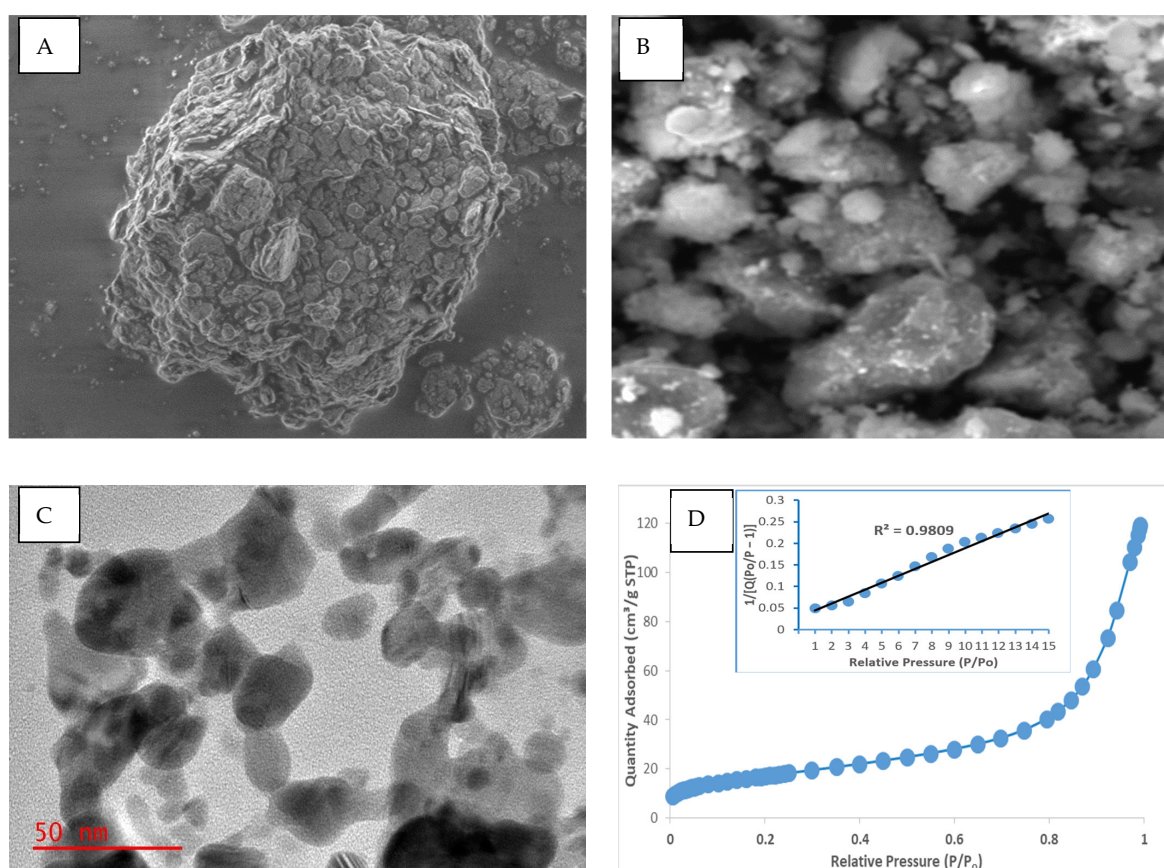


Figure 1. SEM of (A) clay (mag $\times 5000$) and (B) NAgC (mag $\times 20,000$); (C) TEM of NAgC; and (D) BET isotherm and inset of surface area plot of NAgC.

3.2. Elemental Composition Analysis of NAgC

Figure 2A,B illustrates the images of unprocessed clay and NAgC obtained from the SEM (Nova Nano SEM 230, FEI, Hillsboro, OR, USA) microscope equipped with an EDX system (Oxford Instruments NanoAnalysis, High Wycombe, Buckinghamshire, UK). The EDX spectra of NAgC exhibited a clear Ag signal at 2 keV, alongside weaker peaks for silicon (Si), aluminum (Al), iron (Fe), and potassium (K). These weaker peaks hinted at the possible existence of surface biomolecules originating from the *M. esculenta* extract, which was employed in the biosynthesis process. Figure 2B presents the qualitative and quantitative information gathered from the spectra, revealing atomic percentages of 35.3% Ag, 40.3% O, 12.8% Si, 7.4% for Al, 2.0% Fe, and 2.2% C in NAgC. A decrease in silicon percentage within the AgNP compared to the raw clay was observed, ascribed to the organic components in the *M. esculenta* extract. On the other hand, Figure 2A illustrates the raw clay (known as kaolinite, as mentioned in the previous section), consistently showing significant levels of naturally abundant elements (silicon (Si), oxygen (O), and aluminum (Al)), which are inherent in the clay. The lower oxygen level in NAgC compared to the raw clay can be attributed to surface coverage by organic compounds from the *M. esculenta* extract and the reduction of Ag^+ , which reduces the number of surface oxygen-containing groups, similarly reported previously [31–33]. The elemental mapping shown in Figure 2C–H describes the dispersion of the different elements (Fe, Si, Ag, Al, C, and O) present in the NAgC matrix, respectively. This observation buttresses the even distribution of elements captured in the TEM image, which enhances the adsorption capacity of NAgC.

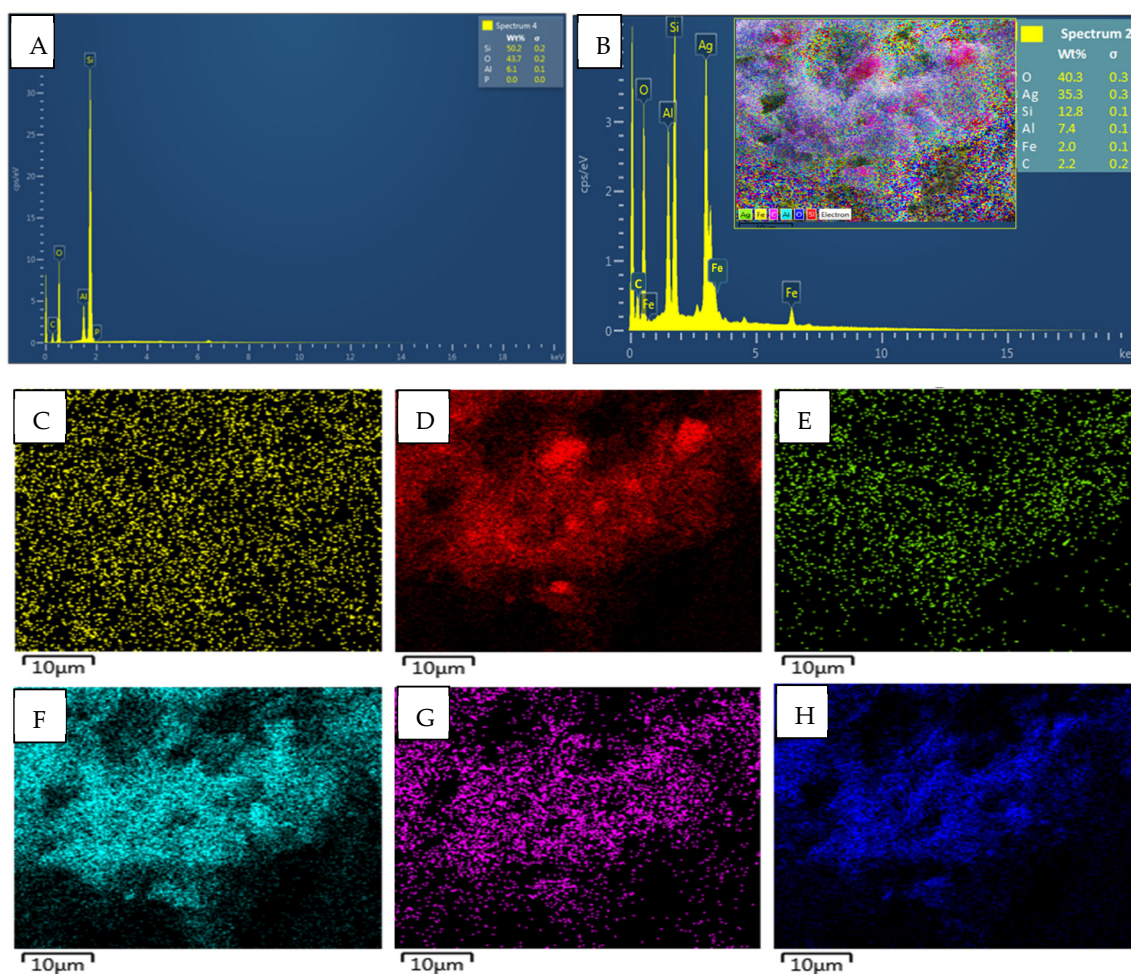


Figure 2. Elemental composition of the (A) raw clay sample, (B) NAgC with inset: electron imaging of (C) Fe, (D) Si, (E) Ag, (F) Al, (G) C, and (H) O.

3.3. Crystallographic Analysis of NAgC

Figure 3A represents the spectrum of pure clay and reveals characteristic peaks indicative of the crystalline phases of its primary constituents, which are typically layered silicates such as kaolinite, montmorillonite, or illite. These peaks, observed at specific 2θ values between $6\text{--}10^\circ$, $20\text{--}30^\circ$, and 40° , are attributed to basal (001) reflections and higher-order planes such as (002) and (110), which are typical of kaolinite-type structures. The low-angle peak ($\sim 6\text{--}10^\circ$) corresponds to the basal spacing arising from the periodic stacking of silicate layers, while the peaks in the $20\text{--}30^\circ$ range are associated with in-plane Si–O and Al–O lattice vibrations, confirming the ordered aluminosilicate framework supported by [21]. Analysis of the basal reflections using Bragg's equation indicates an interlayer spacing (d-spacing) of approximately 1.2–1.4 nm, depending on the specific mineral composition. The sharp and intense nature of these peaks points to a high degree of crystallinity, with minimal structural distortions in the lattice. Furthermore, Scherrer's formula applied to the peak widths suggests an average crystallite size of 30–50 nm, indicating uniform particle size and a highly ordered structure. The absence of significant peak broadening further supports the absence of substantial amorphous phases in the clay sample, as also reported by [23]. In contrast, Figure 3B of NAgC displays significant structural and compositional changes. New peaks appeared at higher 2θ values, of 38.1° , 44.3° , and 64.7° , matching the (111), (200), and (220) planes of the FCC structure of silver nanoparticles, similar to the submission of Bosio et al. [34]. Among these reflections, the (111) plane exhibited the highest intensity, indicating its preferential orientation and confirming the thermodynamically stable growth plane of silver nanoparticles. These peaks align with JCPDS Card number 04–0783, corroborating the crystallinity of NAgC. The calculated average crystallite size using Scherrer's formula was 20 nm, reflecting their nanoscale dimensions. The slight broadening of these diffraction peaks further supports the nanoscale size of the particles and suggests a high surface-to-volume ratio. Additionally, the intensity and sharpness of these new peaks highlight the well-defined and phase purity as supported by a previous work [35]. Comparatively, the spectra show the transformation of the clay upon the incorporation of silver nanoparticles. A noticeable reduction in the intensity of clay-specific peaks suggests partial coverage or interaction of the clay surface by the deposited silver nanoparticles. The reduced intensity of clay-specific peaks, combined with the appearance of distinct silver peaks and changes in d-spacing, indicates a successful integration of silver nanoparticles into the clay matrix [36]. This structural modification confirms the effective dispersion of silver nanoparticles within the clay matrix, which is expected to enhance the surface reactivity and adsorption performance of the nanocomposite.

3.4. Functional Group Elucidation of NAgC

Figure 4A (spectrum of clay) exhibits the characteristic peaks typical of aluminosilicate materials. The broad band observed around 3400 cm^{-1} corresponds to the O–H stretching vibrations from hydroxyl groups and adsorbed water molecules within the clay structure. A peak at 1630 cm^{-1} is attributed to the bending vibrations of H–O–H, further confirming the presence of water in the interlayer regions of clay. The sharp and intense peaks in the range of $1000\text{--}1100\text{ cm}^{-1}$ are associated with Si–O–Si stretching vibrations, a key feature of the silicate framework. Additionally, peaks at $500\text{--}700\text{ cm}^{-1}$ arise from Al–O–Si and Si–O bending vibrations, consistent with the clay's aluminosilicate composition. These peaks confirm the typical structure of natural clay minerals, primarily composed of silica and alumina units.

Figure 4B of NAgC reveals significant changes following the incorporation of silver nanoparticles using *M. esculenta* leaf extract. The broad band near 3400 cm^{-1} diminished in intensity, indicating a reduction in free hydroxyl groups and adsorbed water. This suggests

that an interaction between the silver nanoparticles and the hydroxyl groups on the clay surface aligns with the research findings of some recent works [35,37].

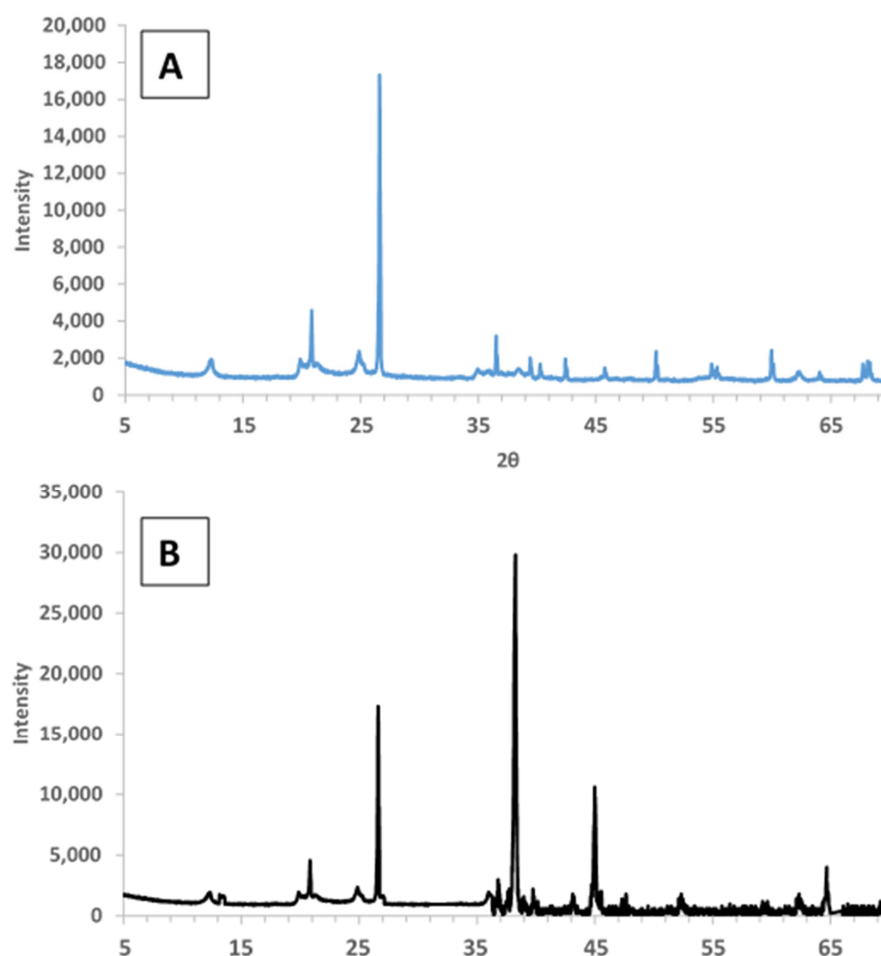


Figure 3. X-ray diffraction analysis of the (A) raw clay sample, and (B) NAgC.

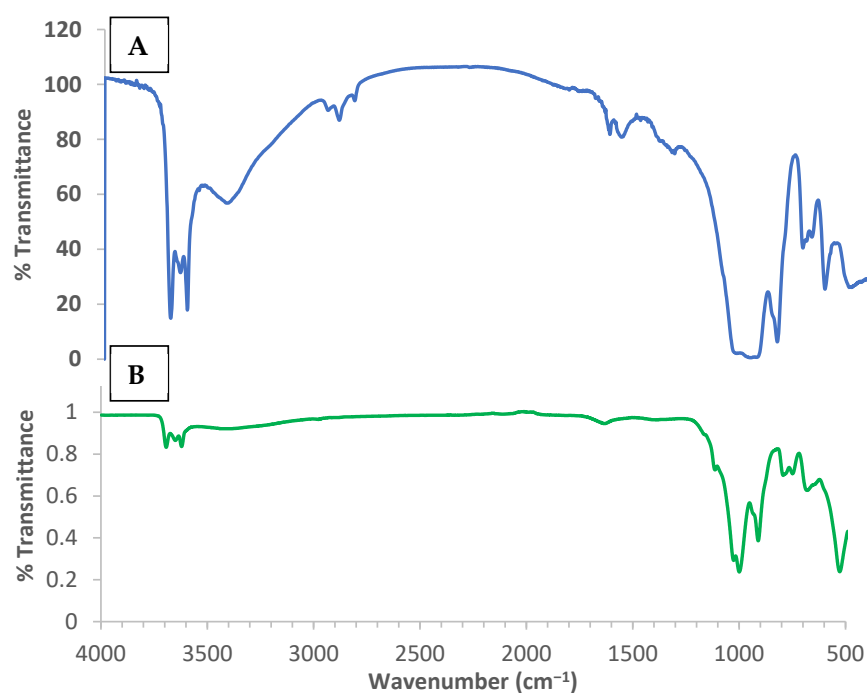


Figure 4. FTIR Analysis of the (A) clay sample and (B) NAgC.

A new peak or enhancement in the range of $1350\text{--}1450\text{ cm}^{-1}$ can be attributed to C–O stretching vibrations, originating from phytochemical compounds (e.g., polyphenols, flavonoids) in the *M. esculenta* extract, which act as both reducing and nucleating agents during nanoparticle synthesis. The band of Si–O–Si stretching around $1000\text{--}1100\text{ cm}^{-1}$ showed reduced intensity and slight shifts, indicative of an interaction between silver nanoparticles and the clay silicate framework and those observed in the range of $500\text{--}800\text{ cm}^{-1}$ were attributed to Ag–O vibrations, confirming the successful formation of silver-based bonds on the clay surface. The appearance of these peaks highlights the role of *M. esculenta* extract in functionalizing the clay surface with silver nanoparticles [35,38].

3.5. Adsorption Studies

The influence of diverse parameters on adsorption efficiency was scrutinized through adsorption studies, and each plays a critical role in the adsorption process.

3.5.1. Effect of Metal Concentration

The initial concentration of heavy metals is a critical factor in the adsorption process, particularly in optimizing removal efficiency. The data presented in Figure 5A clearly demonstrates that both cadmium (Cd(II)) and chromium (Cr(VI)) exhibited an increase in adsorption as their initial concentrations rose, though with notable differences in their adsorption behavior. For Cd(II), as the metal concentration increased from 5 mg/L, there was a significant rise in the quantity adsorbed. Specifically, at 5 mg/L, the quantity adsorbed was 39.09 mg/g, indicating the initiation of effective adsorption. This adsorption capacity increased to 93.04 mg/g at a concentration of 15 mg/L, and further to 131.73 mg/g at 25 mg/L. This trend suggests that as the concentration of Cd(II) increased, the availability of adsorption sites on the AgNC became more fully utilized, resulting in enhanced removal efficiency, a position supported by Asfaram et al. [26].

Similarly, Cr(VI) demonstrated a similar trend in adsorption behavior, although the adsorption values were slightly lower compared to Cd(II). At 5 mg/L, the quantity of Cr(VI) adsorbed was 31.82 mg/g, which was less than that of Cd(II) at the same concentration. As the concentration of Cr(VI) increased to 15 mg/L, the adsorption capacity rose to 80.77 mg/g, and at 25 mg/L, it reached 121.08 mg/g. These findings indicate that Cr(VI) also benefits from increased metal concentration, which enhances the interaction between Cr(VI) ions and the available adsorption sites. The observed differences in adsorption capacity between Cd(II) and Cr(VI) can be attributed to their respective ionic properties and affinities for the functional groups present on the AgNC. The stronger interaction of Cd(II) with the adsorbent, as evidenced by its consistently higher adsorption values, suggests that Cd(II) ions are more effectively captured by the available sites, leading to a more efficient removal process [2]. The metal concentration plays a vital role in determining the adsorption efficiency for both Cd(II) and Cr(VI). However, Cd(II) exhibits a slightly superior adsorption capacity compared to Cr(VI), likely due to its stronger affinity for the adsorbent surface.

3.5.2. Effect of Adsorbent Dosage

The process of determining the most suitable amount of NAgC for capturing specific metal ion concentrations involves systematically adjusting the adsorbent dosage until the most effective quantity is determined. This procedure accomplishes two objectives: it establishes the most efficient amount for metal ion adsorption while balancing economic considerations and effectiveness [39]. As observed in Figure 5B, it is apparent that an increase in the NAgC dosage corresponds to a proportionality in the quantity adsorbed, which corroborates the findings of Asfaram et al. [26]. Interestingly, the optimal dosage was observed at 1 g with an adsorption capacity of 135 and 118 mg/g for Cd(II) and

Cr(VI), respectively, and beyond this point, further increases in dosage do not significantly influence the amount of adsorbed metal ions. As suggested by Afroze et al. [40], this behavior can be ascribed to the presence of an abundant surface area and an ample number of active sites when 1 g of the NAgC is employed. At NAgC dosage levels between 1 and 2 g, a distinct pattern emerges, that interference leads to a plateau in adsorption capacity. This phenomenon mirrors the findings of Pernyeszi and co-workers [41], who noted that higher adsorbent concentrations promote particle collision and agglomeration, resulting in a reduced overall surface area and longer diffusional paths. These combined effects ultimately diminish the sorption capacity of metal ions [41].

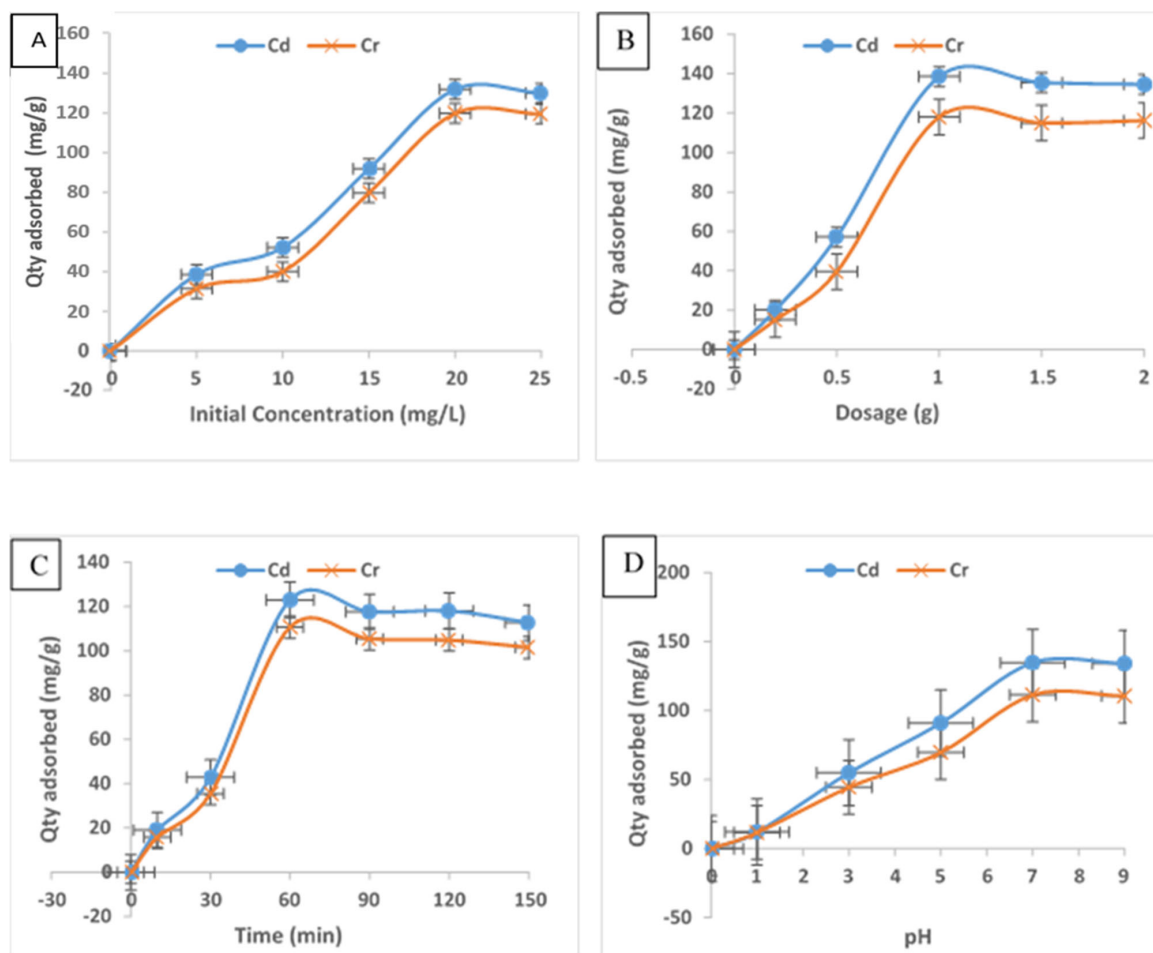


Figure 5. Influence of (A) metal conc. (NAgC = 1 g, contact time = 60 min, pH = 7), (B) NAgC dosage (conc. = 20 mg/L, time = 60 min, pH = 7), (C) contact time (conc. 20 mg/L, NAgC = 1 g, pH = 7), and (D) pH (conc. = 20 mg/L, contact time = 60 min, NAgC = 1 g).

3.5.3. Effect of Contact Time

To comprehend the pace at which Cd^{2+} is taken up by NAgC, an investigation into the duration of contact between the NAgC and the metals (Cd(II) and Cr(VI) ions) was carried out. The effect of contact time on the adsorption of Cd(II) and Cr(VI) onto NAgC (Figure 5C) shows a clear time-dependent uptake pattern characterized by an initial rapid adsorption phase followed by equilibrium. Initially, there was a rapid escalation in Cd(II) and Cr(VI) removal, moving from around 45 mg/g at 30 min to its zenith at 110 and 120 mg/g after 60 min for Cr(VI) and Cd(II), respectively. Subsequently, the process plateaued, establishing an equilibrium point of 100 and around 120 mg/g for Cr(VI) and Cd(II) in that order, as visually represented in Figure 5C. This phenomenon is ascribed to the substantial surface area and presence of vacant sites on NAgC during the initial stages of the adsorption

process, but these sites swiftly became filled up after roughly 60 min of interaction with Cd(II) and Cr(VI). The rapid saturation may arise from steric effects and hindered diffusion by the metal (Cd(II) and Cr(VI)) molecules as the contact time increases, with a similar submission by Moore et al. [42].

3.5.4. Effect of pH

The solution pH has a substantial impact on the adsorption capacity of an adsorbent, and it plays an important function in the solution chemistry, particularly at the interface in the adsorption process [43–45]. In this study, the pH range between 1 and 9 was examined at a Cd^{2+} concentration of 20 mg/L, using 0.1 g of AgNC for a duration of 60 min, as presented in Figure 5D. A direct correlation was observed between the adsorbed quantity and pH levels. Notably, there was a spike in Cd^{2+} adsorption following an increase in pH, reaching its peak at pH 7. This pH-related behavior can be explained by the competitive impact of H^+ on the positively charged Cd^{2+} at the adsorption sites on NAgC, especially in acidic regions. This phenomenon is additionally associated with the greater prevalence of acidic (hydrogen and hydroxonium) ions and the accessible Cd(II) ions [37]. Conversely, a contrasting trend emerged in alkaline pH conditions, where the negatively charged surface-active groups of the NAgC became more pronounced at pH levels exceeding 7. This increased polarization initiated complementary electrostatic interactions between Cd^{2+} ions and the NAgC, resulting in an augmented adsorption capacity.

In contrast to Cd(II), the adsorption behavior of Cr(VI) is strongly influenced by its aqueous speciation, which varies with pH. Under acidic to neutral conditions, Cr(VI) exists primarily as hydrogen chromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), while at alkaline pH, chromate (CrO_4^{2-}) becomes the dominant species. The adsorption of these anionic species onto NAgC is therefore governed by a mechanism that differs from those of cationic metals. At lower pH values, the surface of the NAgC is expected to be relatively protonated, which enhances electrostatic attraction between the positively charged surface sites and negatively charged chromium species, thereby favoring adsorption. As the pH increases, deprotonation of surface functional groups leads to the development of a more negatively charged surface, which would typically result in electrostatic repulsion with chromate ions (CrO_4^{2-}). However, the experimental results indicate that Cr(VI) removal still occurs under these conditions, suggesting that mechanisms other than electrostatic attraction contribute to the adsorption process [45]. This behavior may be attributed to surface complexation involving oxygen-containing functional groups identified by FTIR analysis, as well as the heterogeneous nature of the adsorbent surface, as described by the Freundlich isotherm model in alignment with reports by [35,40,41]. These factors provide multiple interaction pathways, including specific binding sites that can accommodate anionic species. Additionally, the presence of silver nanoparticles may enhance surface reactivity and contribute to adsorption through non-electrostatic interactions. It is important to note that this study did not investigate the potential reduction of Cr(VI) to Cr(III), and therefore, the contribution of redox processes cannot be confirmed. Future studies involving chromium speciation analysis are recommended to further elucidate the dominant removal mechanisms.

3.6. Adsorption Isotherms

An adsorption isotherm describes the underlying interdependence between the adsorbent and adsorbate at a constant temperature [26]. The adsorption performance of the NAgC for cadmium (Cd(II)) and chromium (Cr(VI)) ions, evaluated using the Freundlich and Langmuir isotherm models in Figure 6A,B, provides valuable insights into its behavior and potential applications. Also, Table 1 presents empirical deductions from the isotherm models. The Freundlich constants (K_f) reflect the adsorption capacity at low concentrations,

with values of 0.1259 L/mg for Cd(II) and 0.02552 L/mg for Cr(VI), suggesting a higher affinity of the NAgC for Cd(II) under low-concentration conditions. However, the n values (0.5557 for Cd(II) and 0.4263 for Cr(VI)), both less than 1, indicate that adsorption becomes less favorable at higher concentrations, likely due to limited active sites or competitive interactions. Additionally, the presence of competing ions such as Mg^{2+} and Ca^{2+} may reduce adsorption efficiency to some extent. The high R^2 values (0.9901 for Cd(II) and 0.9977 for Cr(VI)) confirm that the Freundlich model effectively represents the adsorption process, indicating a heterogeneous surface with diverse adsorption energies. The Langmuir model offers complementary insights, emphasizing monolayer adsorption. The maximum adsorption capacity (Q_0) was higher for Cr(VI) (17.8611 mg/g) than Cd(II) (14.9058 mg/g), highlighting NAgC's superior capacity for Cr(VI) adsorption under saturation conditions. Similarly, the Langmuir constant (K_L) was significantly higher for Cr(VI) (0.163 L/mg) compared to Cd(II) (0.020 L/mg), confirming stronger binding interactions for Cr(VI) [46]. Additionally, the R_L values for both metals (0.04 for Cd(II) and 0.06 for Cr(VI)) fell within the range of favorable adsorption ($0 < R_L < 1$), with Cr(VI) exhibiting slightly more favorable adsorption behavior. These findings demonstrate that while NAgC is effective for both metals, its higher Q_0 and K_L values for Cr(VI) make it particularly suited for Cr(VI) remediation. The dual applicability and strong adsorption characteristics of the NAgC underscore its potential to treat water systems contaminated with heavy metals.

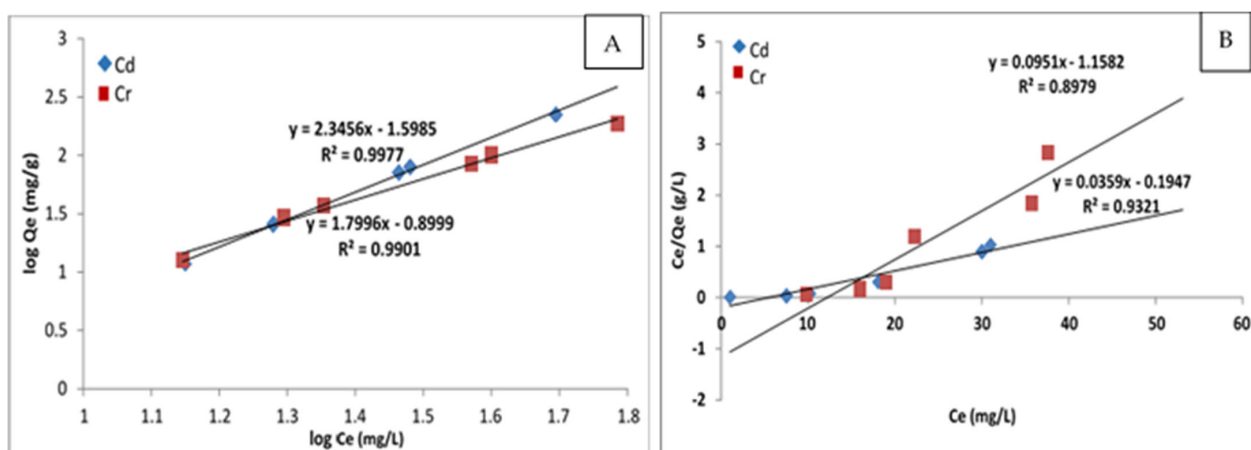


Figure 6. Isotherm models for NAgC. (A) Freundlich; (B) Langmuir.

Table 1. Modeling parameters for the adsorption of Cd(II) and Cr(VI).

Adsorbent	Adsorbate	Freundlich			Langmuir			
		K_f (L/mg)	N	R^2	Q_{0O} (mg/g)	K_L (L/mg)	R_L	R^2
NAgC	Cd(II)	0.1259	0.5557	0.9901	14.9058	0.020	0.04	0.8979
	Cr(VI)	0.02552	0.4263	0.9977	17.8611	0.163	0.06	0.9321

3.7. Kinetic Modelling

The adsorption kinetics of cadmium (Cd(II)) and chromium (Cr(VI)) onto NAgC were evaluated with the PFO and PSO kinetic models, respectively, as shown in Figure 7. The results, as presented in Table 2, provide insights into the time-dependent mechanisms. The PFO model yielded high coefficients of determination (R^2), 0.9984 for Cd(II) and 0.9915 for Cr(VI), indicating a strong fit. The calculated equilibrium adsorption capacities ($Q_{e,cal}$) for Cd(II) and Cr(VI) were 157.87 and 137.91 mg/g in that order. These values aligned well with the experimental observations, suggesting that the adsorption process

may primarily involve physisorption, characterized by the rate-limiting adsorption onto active sites without significant chemical bonding. Conversely, the PSO model exhibited moderately good fits with significantly lower (R^2) values (0.7872 for Cd(II) and 0.7244 for Cr(VI)). The calculated ($Q_{e,cal}$) values for this model were Cd(II), 188.68 mg/g and Cr(VI), 181.12 mg/g, undermining the applicability of this model. Additionally, the PSO rate constants (k_2) were extremely small (7.08×10^{-5} g/(mg·min) and 6.12×10^{-5} g/(mg·min) for Cd(II) and Cr(VI), respectively), indicating a negligible chemisorption process. The better fit of the PFO model suggests that Cd(II) and Cr(VI) transfer onto NAgC is driven predominantly by surface interactions rather than chemisorption mechanisms. This finding underscores the efficiency of the NAgC as a physical adsorbent for heavy metal remediation.

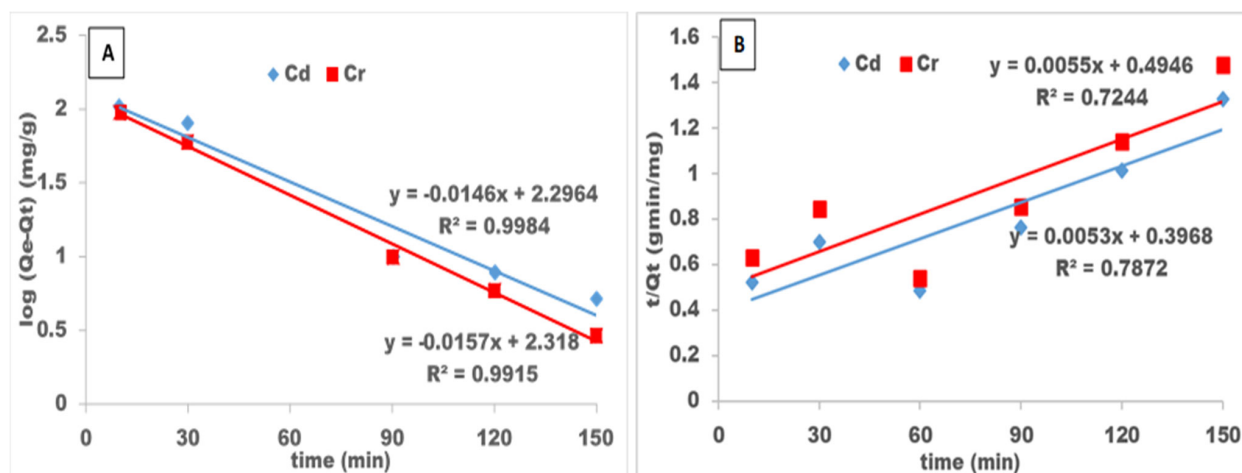


Figure 7. Kinetic plots of the (A) PFO and (B) PSO models for NAgC.

Table 2. Kinetic data for Cd(II) and Cr(VI) adsorption onto NAgC.

Adsorbent	Kinetic Models	Parameters		
			Cd(II)	Cr(VI)
NAgC	PFO	k_1 (min^{-1})	0.0336	0.0362
		$Q_{e,cal}$ (mg/g)	157.87	137.91
		R^2	0.9984	0.9915
	PSO	k_2 (g/(mg·min))	7.08×10^{-5}	6.12×10^{-5}
		$Q_{e,cal}$ (mg/g)	188.68	181.82
		R^2	0.7877	0.7244

3.8. Evaluation of NAgC Regeneration Techniques

The regeneration of nature-based engineered silver-clay nanocomposites (NAgC) for the adsorption of cadmium (Cd(II)) and chromium (Cr(VI)) was systematically investigated to evaluate their efficiency and sustainability for repeated applications as shown in Figure 8. Regeneration techniques, including acid washing, base regeneration, and chelating agent treatment, were employed to desorb the heavy metals and restore the adsorbent's functionality. Acid washing, using HCl, effectively removed Cd(II) and Cr(VI) ions by disrupting their interactions with the adsorbent surface. The initial adsorption capacity of 190 mg/g for Cd(II) decreased progressively to 60 mg/g by the sixth cycle, reflecting the challenges of maintaining adsorption efficiency over multiple regeneration cycles. Although acid washing demonstrated high desorption efficiency initially, the structural integrity of the NAgC showed signs of gradual degradation, likely due to prolonged exposure to acidic conditions. Base regeneration using NaOH solutions facilitated the desorption of Cd(II) and Cr(VI) ions by neutralizing surface charges. This method achieved moderate success, particularly in earlier cycles, but the

adsorption capacity dropped significantly by the fifth and sixth cycles, indicating limitations in its long-term effectiveness, supported by Asfaram et al. [26]. Chelating agents, such as EDTA, exhibited superior desorption efficiency by forming stable, soluble complexes with the metal ions. This approach maintained the structural integrity of the NAgC to a greater extent compared to acid or base treatments, making it a preferred method for extending the operational lifespan of the adsorbent. However, economic and environmental considerations associated with chelating agents required careful assessment. The study revealed that the efficiency of NAgC regeneration decreased progressively with each cycle, underscoring the need for optimization strategies. Combining regeneration methods, such as acid washing with ultrasonic or microwave-assisted techniques, could potentially enhance performance and minimize structural deterioration. These findings contribute to advancing the application of nanocomposite adsorbents in environmental remediation.

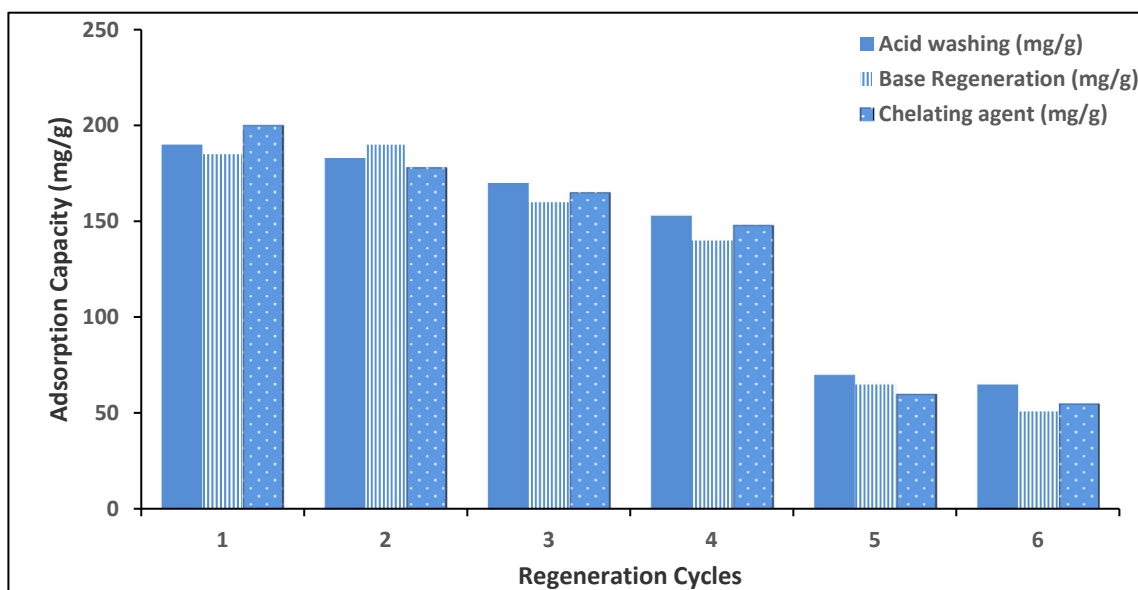


Figure 8. Efficiency of NAgC regeneration techniques.

As presented in Table 3, the adsorption performance of silver-based nanocomposites is strongly governed by both material design and the dominant removal mechanism reported in each study. For Cr(VI), Gonfa et al. [27] demonstrated that AgNP–diatomite exhibits a relatively low capacity (10.99 mg/g), which they attributed to limited surface functionalization and a mechanism dominated by surface adsorption. In contrast, Zouggari et al. [47] reported a significantly higher capacity (149.76 mg/g) for Cys-PPy@Ag₃PO₄, where the performance was linked to the presence of cysteine functional groups and the conductive polypyrrole matrix, facilitating both electrostatic attraction and the redox transformation of Cr(VI). A similar enhancement was observed in the Ag/Fe⁰-activated carbon system (PAC-Fe⁰/Ag), where Kakavandi et al. [33] reported a capacity of 100 mg/g. Their study emphasized that zero-valent iron plays a critical role in reducing Cr(VI) to Cr(III), while activated carbon provides a high surface area for subsequent adsorption. For Cd(II), Nyirenda et al. [48] reported a capacity of 87.72 mg/g for AC–Ag–SiO₂, attributing this to the improved dispersion of Ag nanoparticles and the synergistic effect of silica in stabilizing the composite structure and enhancing pore accessibility.

Higher adsorption capacities are observed in biopolymer-based systems. Chaudhry et al. [49] reported an exceptionally high $q_{\max}$ of 354.61 mg/g for chitosan-based hydrogels, which they associated with the high density of amine and hydroxyl functional groups and the swelling behavior of the hydrogel that increases metal ion diffusion and accessibility to binding sites. Similarly, Khan et al. [50] demonstrated that chitosan-capped Ag

nanoparticles achieved 119.04 mg/g due to improved nanoparticle stabilization and the increased availability of active binding sites. In comparison, the NAgC developed in this study showed adsorption capacities of 133.7 mg/g for Cd(II) and 121.4 mg/g for Cr(VI), which are consistent with systems where both adsorption and surface-mediated reduction are operative. The relatively high performance can be reasonably attributed to the presence of phytochemical functional groups introduced during plant-mediated synthesis, which likely enhance metal binding and electron transfer, as described elsewhere [35,40]. The combination of sustainable synthesis techniques with high removal efficiency makes this nanocomposite particularly relevant.

Table 3. Comparison of different synthesis techniques, targeted contaminants, and percentage removal with the current study.

Nanocomposite	Method of Synthesis	Target Contaminant(s)	Adsorption Capacity, $q_{\max}$ (mg/g)	Ref.
AgNP–diatomite (AgNP–DE)	Impregnation/reduction	Cr(VI)	10.99	[27]
Ag/Fe ⁰ –activated carbon (PAC–Fe ⁰ /Ag)	Chemical reduction + impregnation	Cr(VI)	100.00	[34]
Cysteine-polypyrrole@silver phosphate (Cys–PPy@Ag ₃ PO ₄) nanocomposite	Chemical polymerization	Cr(VI)	149.76	[47]
Activated carbon–Ag–SiO ₂ nanocomposite (AC–Ag–SiO ₂)	Impregnation + composite synthesis	Cd(II)	87.72	[48]
Chitosan-based hydrogels	In situ free-radical polymerization + covalent crosslinking + interpenetrating network formation	Cd(II)	354.61	[49]
Chitosan-capped silver nanoparticles (Chi–Ag)	Chemical reduction	Cd(II)	119.04	[50]
NAgC	Plant-mediated synthesis	Cd(II) Cr(VI)	157.87 137.91	This study

4. Conclusions

This study demonstrates the efficacy of a nature-based engineered silver-clay nanocomposite (NAgC), synthesized using *Manihot esculenta* leaf extract, for the removal of cadmium (Cd(II)) and chromium (Cr(VI)) ions from drinking water with potential application in Akwa Ibom State, Nigeria. Characterization of the NAgC revealed enhanced adsorption properties due to its mesoporous structure, increased surface area, and functionalization by phytochemicals from the plant extract. Adsorption efficiencies were dependent on initial metal concentration, NAgC dosage, solution pH, and contact time. The adsorption and kinetic data were adequately interpreted by the Freundlich and PFO kinetic models, respectively. These results underscore the potential of the NAgC as a cost-effective and sustainable alternative for water remediation, especially in some polluted surface waters. One limitation of this study was the use of AAS, which, despite its sensitivity and reliability for single-element analysis, is limited in comparison to advanced techniques such as inductively coupled plasma-optical emission spectroscopy (ICP-OES). Furthermore, adsorption experiments were conducted under single-component conditions, and thus do not capture the competitive effects inherent in multicomponent adsorption systems.

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E.J.I., D.P.F., N.A.A. and N.-A.O.O.; visualization, S.E.S., N.S.E., N.D.I. and N.-A.O.O.; supervision, S.E.S. and E.J.I.; funding acquisition, S.E.S. and E.J.I. All authors have read and agreed to the published version of the manuscript.

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