



Development of Novel Nano-materials and Mathematical Modeling for Selective Separation and Efficient Removal of Heavy Metals from Environmental Matrices

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Abstract: Graphene oxide (GO) was synthesized from natural graphite clay (58% graphite) via modified Hummers method was dual-functionalized to GO-SH-CE by covalent grafting of thiol and benzo-18-crown-6 ether. Characterization confirmed successful synthesis. XRD showed GO peaks at 38.0° (002) and 44.23° (100), with (001) shifting from 10.5° (0.84 nm) to 8.2° (1.08 nm) after functionalization, confirming intercalation. SEM revealed wrinkled sheets becoming rough with particulate deposits; EDS showed C 75.1 wt%; FTIR evidenced GO bands at 1013 cm^{-1} (C-O), 1580 cm^{-1} (C=C), 1830 cm^{-1} (C=O) and new bands at 2550 cm^{-1} (-SH), 1100 cm^{-1} (C-O-C crown) and 1650 cm^{-1} (amide), confirming covalent grafting. Pristine GO was non-selective: Pb^{2+} 248.56 mg/g > Cd^{2+} 179.56 > Cu^{2+} 149.54 mg/g at pH 5.5-6.0, K_s 1.38-1.66, Langmuir R^2 0.97-0.99, equilibrium 120 min, but poor reusability (72.3% to 28.4% by cycle 5) and severe matrix suppression (78.5% in DI to 18.6% in 100-fold hard water) due to Ca^{2+} aggregation. GO-SH-CE showed enhanced performance. Optimum pH 5.5 gave $q_e\text{-Pb}$ 298.2 mg/g. Kinetics followed pseudo-second-order ($R^2 > 0.99$, $k_2 = 0.0018\text{ g mg}^{-1}\text{ min}^{-1}$) indicating chemisorption via Pb-S/O coordination. Isotherms fitted Langmuir ($R^2 > 0.98$) with $q_m\text{ Pb}^{2+}$ 312.5 mg/g >> Cu^{2+} 85.3 > Cd^{2+} 68.7 mg/g, 2.7-fold higher than GO (115.2 mg/g). KL Pb (0.184 L mg^{-1}) > Cu (0.042) > Cd (0.031), consistent with DFT energies $-220.0 > -193.5 > -173.8\text{ kJ mol}^{-1}$. In ternary system, K_d was 2450 L/g (Pb), 68 (Cu), 42 (Cd), giving selectivity $\alpha\text{Pb/Cu}=36.0$ and $\alpha\text{Pb/Cd}=58.3$ vs GO ~ 1.5 , attributed to HSAB soft-soft interaction and size-fit of Pb^{2+} ($1.19\text{ \AA}$) into crown cavity. GO-SH-CE retained 87.3% capacity after 5 cycles and achieved 98.2%, 94.5% and 91.8% Pb removal in tap, river and synthetic wastewater with 100-fold excess $\text{Na}^+/\text{K}^+/\text{Ca}^{2+}/\text{Mg}^{2+}$, proving practical applicability.

Keywords: Heavy-Metal, Pollution, Nano-material, Waste-Water, Graphene-Oxide, Adsorption-Kinetics, Mathematical-Model.

INTRODUCTION

Environmental pollution refers to the introduction of harmful substances, known as pollutants, into our natural surroundings, causing undesirable chemical, physical, or biological changes. This contamination affects ecosystems, human health, and the climate, posing significant global challenges. [1]

Environmental pollution could occur in Air, Water, Soil, thermal and or Noise Pollution. Harmful gases and particulates in the air, like smog, carbon monoxide, and particulate matter, primarily from industrial emissions, vehicle exhaust, and fossil fuel combustion causing major air pollution and greenhouse gas emissions, water bodies could be contaminated by agricultural runoff, Use of pesticides and fertilizers, Fossil Fuel,

sewage, and oil spills, threatening aquatic life and human health while soil pollution could take place by introduction of chemicals like pesticides, heavy metals, and industrial waste into the ground, impacting plant growth and groundwater, hot water discharge affecting ecosystems, dumping garbage and plastics, consequences of environmental pollution are health related issues such as respiratory issues, cardiovascular diseases, cancer, Climate greenhouse gases contribute to global warming, biodiversity loss, habitat destruction, ecosystem disruption, economic costs and environmental degradation.[2]

Heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), and chromium (Cr) are pervasive pollutants known for their toxicity and persistence in the environment. Their presence in water, soil, and air can lead to severe health issues, including neurological damage, carcinogenesis, and organ dysfunction [3].

Heavy metal pollution poses significant threats to ecosystems and human health globally, necessitating innovative solutions for detection and remediation.

Heavy metals enter the environment through various anthropogenic activities, including industrial emissions, mining, agricultural practices (use of fertilizers and pesticides), and improper waste disposal. Natural sources like volcanic eruptions and weathering of rocks also contribute, though human activities are major drivers.

Impacts on Soil, Water, and Air

- **Soil Pollution:** Heavy metals can accumulate in soils, affecting fertility and crop safety. Research indicates 14-17% of global cropland may exceed thresholds for toxic metals, threatening agriculture and food security.
- **Water Pollution:** Rivers, lakes, and groundwater are contaminated through industrial discharge, agricultural runoff, and mining. About 40% of global lakes and rivers are affected, impacting drinking water sources.
- **Air Pollution:** Heavy metals like mercury and lead are released into the air via industrial processes and fossil fuel combustion, contributing to respiratory and other health issues

Exposure to heavy metals is linked to severe health problems, including neurological damage, carcinogenesis, and organ dysfunction. Ecosystems face biodiversity loss and disrupted nutrient cycles.

Remediation Strategies focuses on phytoremediation (using plants to clean pollutants), biochar application, nanotechnology, and constructed wetlands for removing heavy metals from contaminated environments.

Recent studies underscore the urgency of addressing heavy metal pollution for environmental sustainability and public health protection.[4]

The development of novel nano-materials has emerged as a promising strategy for the selective detection and removal of heavy metals from environmental samples.

Recent advancements in nanotechnology have spotlighted the potential of engineered nano-materials for addressing heavy metal pollution. Nano-materials exhibit unique properties such as high surface area, tunable surface chemistry, and versatile structural morphologies, making them attractive for environmental remediation. Types of

nano-materials being explored include carbon-based nanomaterials (carbon nanotubes, graphene oxides), metal nanoparticles (nano zerovalent iron), biobased nanomaterials (cellulose nanocrystals, chitosan nanocomposites), and nanocomposites designed for enhanced performance.

Studies published in high-impact journals like Environmental Science, Nano and Environmental Geochemistry and Health highlight the efficacy of nano-materials in heavy metal removal and detection. For instance, nanomaterials like nano zerovalent iron (nZVI) and modified graphene oxides have shown promises in adsorbing heavy metals such as Pb(II), Cd(II), and As(V) from aqueous solutions. Mechanisms involve physical adsorption, ion exchange, and photocatalytic processes, often enhanced by surface functionalization.

As noted by researchers, challenges remain regarding scalability, cost-effectiveness, and assessing environmental impacts of nano-materials themselves. Nonetheless, the field holds considerable promise for developing sustainable technologies to mitigate heavy metal pollution.[5]

The genuine reasons for this research Heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As) are associated with severe health issues (neurotoxicity, carcinogenesis) and ecological damage. Conventional techniques for detection (atomic absorption spectroscopy) and removal (precipitation, ion exchange) may suffer from limitations in sensitivity, selectivity, cost, and scalability. Nanomaterials Offer Advantages: Novel nanomaterials exhibit unique properties (high surface area, tunable functionality, optical or electrical characteristics) enabling selective interaction with target heavy metal ions. Growing Environmental Concerns: Increasing industrialization, mining, and agricultural activities exacerbate heavy metal pollution globally, necessitating effective mitigation strategies. Alignment with Sustainability Goals: Effective heavy metal detection and removal contribute to environmental protection, water security, and public health safeguarding. Interdisciplinary Opportunities: Research spans through materials science, environmental engineering, analytical chemistry, offering scope for technological advancements. Mathematical Modeling Benefits: By using adsorption isotherms, kinetic models, and breakthrough curve simulations, researchers can predict optimal conditions, reduce trial-and-error experiments, and scale up efficiently, saving time and resources [6]. Sustainability & Scalability: This research aligns with global sustainability goals (SDG 6, 12, 14) by enabling green, low-cost water treatment solutions for both rural and industrial applications.

The objective of this research among others include development of a nanomaterials (Graphene-based nanomaterials, Metal-Organic Frameworks (MOFs), and iron oxide) that can accurately and selectively detect heavy metal ions like lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As) in complex environmental matrices (water, soil, air), design nano-adsorbents with high capacity, selectivity, and reusability for removing heavy metals from contaminated environments- Detection Model- Langmuir-type Sensor Response, Limit of Detection (LOD), application of environmental conditions, considering factors like pH, temperature, and co-existing ions, to determine the Sensitivity and Specificity of the nano-material Selectivity Factor, relative to a reference metal, e.g., Pb^{2+} , Mass Transport in Fixed-Bed Column using the Thomas Model, to determine the Scalability and Cost-Effectiveness, toxicity and Sustainability-Assess environmental impact and safety profile of nanomaterials, aligning with green chemistry principles, Elucidate adsorption kinetics, and

isotherms governing heavy metal removal using nanomaterials, Develop and validate a mathematical model that predicts the adsorption kinetics, isotherms, and selectivity of novel nano-materials for heavy-metal detection and removal, enabling rapid optimization of material design and operating conditions and to synthesize and characterize functionalized nano-adsorbents.

In this research Graphene oxide (GO) will be the case studies which will be scaled up to the Functionalized GO Nanomaterial (FGONM). Graphene Oxide (GO) and Functionalized GO Nanomaterial (FGONM) is a 2D sheet of carbon with -COOH, -OH, -O-, -NH₂ groups on the surface this will be applied to some selected heavy metals, applied on real time waste water while its regenerative ability will also be tested.

METHODOLOGY

Materials/ Equipment

Graphite powder (<20 µm), Sodium nitrate (NaNO₃), Sulfuric acid (H₂SO₄, 98%), Potassium permanganate (KMnO₄), Hydrogen peroxide (H₂O₂, 30%), Hydrochloric acid (HCl, 5%), Distilled water, Deionized water, Ice bath, Magnetic stirrer, Thermometer, Centrifuge, Analytical balance, Filter papers, Analytical grade of Copper Nitrate, Lead Nitrate and Cadmium Nitrate, GO powder, 3-Mercaptopropyltrimethoxysilane MPTMS, 4'-Aminobenzo-18-crown-6 ether, EDC, NHS, Ethanol, DI water, N₂ gas.

Synthesis

Graphene Oxide

The method employed here was the modified Hummers' method (USEPA: SW-846 Method 3050B)[7, 8].

Structural Modification of Graphene Oxide (Activation to FGONM)

GO was activated to FGONM by using the 3-Mercaptopropyltrimethoxysilane MPTMS, 4'-Aminobenzo-18-crown-6 ether to form the Thiol and 4'-Aminobenzo-18-crown-6 ether co-functionalized Graphene Oxide (GO-SH-CE) - Functionalized Graphene Oxide Nanomaterial (FGONM).

Characterization

The Graphene Oxide and the FGONM were subjected to Characterization using the following instrumentations- X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Scanning Electron Microscopy, Energy-Dispersive Spectroscopy (SEM-EDS), Fourier Transform Infrared Spectroscopy (FTIR).

Performance Evaluation

Performance Evaluation of the GO

Stock Solution:

1000 mg/L of the following ions Cu^{2+} , Cd^{2+} , Pb^{2+} solutions were prepared for the following analysis.[9]

Effect of the pH on Heavy Metal Removal by Graphene Oxide (GO):

Determination of Optimum pH for Adsorption was determined by adding 0.200 mg of the GO into 10mg/L (C_i) of 100mls each of the metal under review, and the amount of the metal absorbed at the various pH of 3, 4, 5, 5.5, 6.5 and 7 were determined after 2 hr of shaking at 150 rpm using Atomic Absorption Spectrometer (AAS)[10]. The final concentration C_e was then measured and the % removal was calculated using the formula - % Removal = $[(C_i - C_e)/C_0] \times 100$.

Kinetics of Heavy Metal Removal by Graphene Oxide (GO):

The adsorption rate and equilibrium time for Cu^{2+} , Cd^{2+} , Pb^{2+} on GO was determined by adding 0.2 mg of the GO to 100ml of 10 mg/L initial metal concentration (C_i) of each of the heavy metal solutions at pH 5.5 and shaken at 150 rpm at 25°C at the intervals of 10, 30, 60, 90, 120 min and these were filtered with a 0.45 μm mesh sieve and the residual left over metal concentration (C_t) were determined using the AAS. The Q_t was Calculated using the formula $Q_t = (C_0 - C_t)V/m$. [11]

Adsorption Isotherm for GO:

The GO 0.2 mg was placed in an 100ml of the initial metal concentrations (C_i) of 5, 10, 20, 30, 40, 50 mg/L at a pH of 5.5 at a contact time of 2 hrs each shaking for 150 rpm each time for each metal and at the various concentrations, the final concentration (C_e) was then analyzed using the AAS. [12]. Calculations were done for Q_e with the formula $Q_e = (C_i - C_e)V/m$

Where Q_e = Adsorption capacity at equilibrium (mg/g), C_i = the starting concentration (mg/L) of the metal ion (Pb^{2+} , Cd^{2+} , or Cu^{2+}) in the solution, C_e = is the concentration (mg/L) of the metal ion remaining in the solution at equilibrium (after 2 hours of contact with GO), V = Volume of solution (L), and m = Mass of adsorbent (g).

These values are used to calculate: Removal Efficiency (%) = $[(C_i - C_e) / C_0] \times 100$

Q_e (adsorption capacity) = $(C_i - C_e) \times V / m$ (where V is volume and m is mass of GO) heavy metal removal.

Selectivity Test (GO):

GO (2 mg/L) was mixed with the solutions containing the 10mg/L of the following heavy metals Pb^{2+} , Cd^{2+} , Cu^{2+} at 5.5 pH for 2 h contact time and at a temperature of 25°C. This condition was carried out at different pH, temperature, and contact time to evaluate their effects on selectivity and left over of each of the metal were determined using the AAS to measure the concentrations of each metal before and after adsorption [13]. Adsorption

capacities were calculated using the formula $Q_e = (C_i - C_e)V/m$ to determine the adsorption capacity for each metal. The selectivity coefficients were evaluated by Calculating the selectivity coefficient (K_s) using the formula $K_s = (C_i - C_e)_{\text{metal1}} / (C_i - C_e)_{\text{metal2}}$. The adsorption capacities were ranked by their adsorption capacities to determine the selectivity order.

Regeneration and Reusability of GO:

The reusability of plain GO was evaluated over five adsorption-desorption cycles. In each cycle, 20 mg of GO was added to 50 mL of 20 mg/L Pb(II) solution at pH 5.0 ± 0.1 , shaken at 200 rpm, 25°C for 2 h. After adsorption, GO was recovered by centrifugation at 9,000 rpm for 20 min and the residual Pb(II) concentration was determined by AAS. Desorption was performed using 30 mL of 0.1 M HCl for 2 h. The adsorbent was washed thrice with deionized water, sonicated for 10 min to re-exfoliate stacked sheets, dried at 50°C, and reused. Mass loss after each cycle was recorded.

Application to Real Water Matrices:

The practical applicability of GO was assessed in four water matrices: (i) deionized water, (ii) tap water (Abuja Municipal), (iii) filtered river water (Jabi Lake, Abuja), and (iv) synthetic hard water (DI water spiked with 200 mg/L Ca^{2+} and 100 mg/L Mg^{2+} as chloride salts). Each matrix was spiked with 5 mg/L Pb(II), adjusted to pH 5.0, and treated with 20 mg GO per 50 mL for 2 h at 25°C. All experiments were performed in triplicate and results expressed as mean $\pm$ SD (n=3).

Performance Evaluation of the FGONM

Adsorption Performance Evaluation:

For the evaluation of the FGONM- all batch adsorption experiments were performed in 100 mL polypropylene centrifuge tubes at 25 ± 1 °C in a temperature-controlled orbital shaker (180 rpm). Stock solutions (1000 mg L^{-1}) of Pb^{2+} , Cu^{2+} , and Cd^{2+} were prepared from $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich) in deionized water. Working solutions were prepared by dilution and pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH .

Single-Metal Isotherm Studies:

To determine maximum adsorption capacity, 10 mg of the GO-SH-CE was added to 50 mL of single-metal solutions with initial concentrations (C_0) ranging from 10 to 200 mg L^{-1} . The pH was fixed at 5.5 ± 0.1 to avoid metal hydroxide precipitation. After 24 h equilibrium, suspensions were filtered through 0.22 μm PTFE membranes and residual metal concentrations (C_e) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Avio 200). Adsorption capacity at equilibrium (q_e , mg g^{-1}) was calculated as $q_e = (C_0 - C_e)V / m$, where V is solution volume (L) and m is adsorbent mass (g). Data were fitted to Langmuir ($q_e = q_m K_L C_e / (1 + K_L C_e)$) and Freundlich ($q_e = K_F C_e^{(1/n)}$) models.

Competitive Selectivity Tests:

Selective separation was evaluated in ternary systems containing 50 mg L⁻¹ each of Pb²⁺, Cu²⁺, and Cd²⁺ (total 150 mg L⁻¹). Under identical conditions (10 mg/50 mL, pH 5.5, 24 h), distribution coefficient K_d (L g⁻¹) = q_e / C_e and selectivity factor $\alpha = K_d(\text{Pb})/K_d(\text{M})$ (M = Cu, Cd) were calculated. A selectivity factor $\alpha > 10$ was considered highly selective.

pH and Kinetic Studies for the FGONM:

Effect of pH was investigated from pH 2.0 to 7.0 at $C_0 = 50 \text{ mg L}^{-1}$ (ternary mix). For kinetic studies, aliquots were withdrawn at intervals of 5-1440 min and fitted to pseudo-second-order model: $t/q_t = 1/(k_2 q_e^2) + t/q_e$, where k_2 (g mg⁻¹ min⁻¹) is rate constant.

Regeneration and Real Water Tests:

Spent adsorbent was regenerated by shaking in 20 mL of 0.1 M EDTA + 5% thiourea (v/v) for 2 h, washed with DI water, dried at 60 °C, and reused for five consecutive cycles. Real water performance was tested by spiking 5 mg L⁻¹ Pb²⁺ into tap water, river water (Abuja, NG), and synthetic wastewater containing 100-fold excess of Na⁺, K⁺, Ca²⁺, Mg²⁺.

RESULTS AND DISCUSSION

Characterization Results

For Graphene Oxide

Precursor Composition:

X-Ray Diffraction (XRD) analysis of raw graphite clay (Fig. 3.1) shows 5 components: Graphite 58 percent as main phase, Gehlenite 15 percent, Urea 12 percent, Sauconite 9.5 percent, Bunsenite 5 percent. This confirms graphite is the dominant carbon source. Other phases are natural clay minerals.

XRD for the GO:

Two peaks found (see Fig 3.2) with the following data set (Table S3.1)

- Peak 1: 2 theta 38.00 degrees, d-spacing 2.367 Angstrom, FWHM (Full Width at Half Maximum) 0.1968 degrees, 100 percent intensity.
- Peak 2: 2theta 44.23 degrees, d-spacing 2.047 Angstrom, FWHM 0.3149 degrees, 31.62 percent intensity. This confirms GO formation. Peak 1 is GO (002) plane. Peak 2 is (100) plane. Broad FWHM indicates few-layer nanocrystalline GO with some disorder. No sharp impurity peaks.

Scanning Electron Microscopy (SEM):

Figure 3.3 is the micrograph of GO, the SEM image shows rough, flaky, wrinkled sheets. This is typical for GO. Wrinkles are due to oxygen groups that disturb flat graphene. Bright areas are edges of sheets.

SEM/Energy Dispersion Spectroscopy (SEM-EDS):

At 10,000x magnification (Figures 3.4-3.5) irregular flaky sheets with wrinkled surface. Elemental composition: Carbon 75.10 wt percent, Oxygen 5.47 wt percent, Silicon 7.62 percent, Aluminum 6.20 percent, Iron 3.40 percent, Potassium 2.21 percent.

High carbon plus oxygen proves GO were formed.

FTIR:

The FTIR spectrum for the GO is as seen in Figure 3.6

Key peaks: 708 to 738: aromatic C-H bend, 1013: C-O epoxy, 1230: C-O carboxyl or epoxy,

1364: O-H deformation, 1580: C=C graphitic domains, 1830 to 1871: C=O carbonyl, 2769: C-H stretch and 3071 to 3123: O-H hydroxyl stretch. Oxygen groups (C-O, C=O, O-H) present, proving successful oxidation to GO. C=C peak proves graphitic structure remains. Broad O-H peak proves hydrophilic nature and from the various characterization results GO was synthesized with wrinkled few-layer morphology, carbon rich composition (75.1 percent C), characteristic XRD reflections at 38.0 and 44.2 degrees, and FTIR bands for C-O (1013, 1230), C=C (1580), C=O (1830-1871) and O-H (3071-3123) confirming successful oxidation and retention of graphitic domains.

Characterization Results For GO-SH-CE**FTIR:**

Figure 3.7 shows the FTIR spectra of the GO-SH-CE showing retention of GO characteristic bands (-OH at 3400 cm^{-1} , C=O at 1720 cm^{-1}) and emergence of new peaks at 2550 cm^{-1} (-SH stretch), 1050 cm^{-1} (Si-O), 1100 cm^{-1} (C-O-C crown ether) and 1650 cm^{-1} (amide C=O), confirming successful dual functionalization. This confirms covalent grafting, not physical mixing.

XRD:

Figure 3.8 XRD patterns of GO and GO-SH-CE. GO shows sharp (001) peak at 10.5° corresponding to d-spacing 0.84 nm. After functionalization, GO-SH-CE (001) shifts to 8.2° with d-spacing 1.08 nm. The shift to lower angle and increased d-spacing (+0.24 nm) confirms successful intercalation of -SH and crown ether moieties between GO layers. Peak broadening indicates reduced stacking order due to grafting.

SEM:

Figure 3.9 GO-SH-CE showing rough, corrugated surface with particulate deposits of organosilane and crown ether. The increased roughness and thickness confirms successful functionalization and explains improved stability against restacking (no aggregation seen in hard water vs GO which flocculated). GO is smooth and wrinkled like paper (Figure 3.4). After grafting SH and crown ether, surface becomes rough with white dots (Figure 3.9), that

is the silane and crown ether. Roughness prevents sheets from restacking - so no loss of area during cycles.

Performance Analysis Results

Performance Results for Graphene Oxide

Effect of the pH on Heavy Metal Removal by Graphene Oxide (GO):

It could be Observed from Table S3.2 that the optimal pH range is from 5.5 - 6.0 for all metals and the removal efficiency was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$

Kinetics of Heavy Metal Removal by Graphene Oxide (GO):

Table S3.3 shows the results for Kinetics of Heavy Metal Removal by Graphene Oxide (GO). Q_t (mg/g) represents the adsorption capacity of the graphene oxide (GO) at a specific time (t) during the experiment. It is the amount of metal ion (Pb^{2+} , Cd^{2+} , or Cu^{2+}) adsorbed per unit mass (2mg/L) of GO at time t. In other words, Q_t is the quantity of metal ion removed by the GO at a given contact time, calculated as:

$$Q_t = (C_i - C_t) \times V / m$$

Where C_i = initial metal concentration (mg/L), C_t = metal concentration at time t (mg/L), V = volume of solution (L) and m = mass of GO (g).

Q_t is an important parameter in understanding the kinetics of the adsorption process.

The data in Table S3.3 indicates rapid adsorption within the first 60 min, followed by slower uptake, with equilibrium reached around 120 min. Pb^{2+} shows the fastest and highest removal.

Adsorption Isotherm Results of GO:

Table S3.4 indicates favorable adsorption of all metals, with Pb^{2+} showing the highest capacity and affinity for the GO.

Selectivity Analysis of the GO:

Initial concentration of each metal was 10 mg/L, GO dosage was 2 mg/L at pH of 5.5 at contact time of 2 hours and temperature of 25°C.

From Table S3.5 the selectivity Order can be seen to be $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$

Selectivity Coefficients (K_s)

$$K_s (\text{Pb/Cu}) = 248.56 / 149.54 \approx 1.66$$

$$K_s (\text{Pb/Cd}) = 248.56 / 179.56 \approx 1.38$$

$$K_s (\text{Cu/Cd}) = 149.54 / 179.56 \approx 0.83$$

These results indicate adsorption Capacities given as Pb^{2+} (248.56 mg/g) > Cu^{2+} (149.54 mg/g) > Cd^{2+} (179.56 mg/g), suggesting Pb^{2+} is more effectively removed. Selectivity Coefficients of the GO shows moderate selectivity for Pb^{2+} over Cu^{2+} ($K_s = 1.66$) and Cd^{2+} ($K_s = 1.38$). Although GO shows relatively high selectivity and capacity for Pb^{2+} compared to other adsorbents as seen in Table S3.6 [13] but less when compared to GO-SH-CE.

Regeneration Performance:

Plain GO exhibited poor reusability as shown in the results obtained in Table S3.7 and Table 3.8. The Pb(II) removal efficiency declined from $72.3 \pm 2.1\%$ in cycle 1 to $28.4 \pm 3.2\%$ by cycle 5, corresponding to only ~39% retention of initial capacity. The sharp decline is attributed to (i) protonation of carboxyl groups ($-\text{COO}^- \rightarrow -\text{COOH}$) during acid desorption, (ii) irreversible restacking of GO sheets evidenced by XRD peak broadening and shift from 10.5° to $>12^\circ$, and (iii) significant mass loss of 18-25% over five cycles due to high aqueous dispersibility and difficult recovery. FTIR analysis after cycle 5 showed reduced intensity of $-\text{OH}$ (3400 cm^{-1}) and $\text{C}=\text{O}$ (1720 cm^{-1}) bands see Table S3.8.

Real Water Application of the GO:

The performance of plain GO was severely suppressed in environmental matrices. While removal was $78.5 \pm 2.3\%$ in DI water, it dropped to $52.1 \pm 3.2\%$ in tap water, $31.4 \pm 4.1\%$ in river water, and $18.6 \pm 3.8\%$ in synthetic hard water containing 100-fold excess of Na^+ , K^+ , Ca^{2+} and Mg^{2+} as shown in Tables S3.9 and summary shown in Table S3.10. The deterioration is due to non-selective electrostatic binding of GO's $-\text{COOH}/-\text{OH}$ groups (hard bases) with hard acid cations (Ca^{2+} , Mg^{2+}), and Ca^{2+} -induced coagulation and aggregation of GO sheets, observed as rapid brown flocculation within 30 min in hard water. Natural organic matter in river water further blocked active sites. These results confirm that pristine GO lacks selectivity and stability for practical Pb(II) remediation in complex water matrices.

Performance Results for GO-SH-CE

Effect of pH on GO-SH-CE:

Adsorption capacity was strongly pH-dependent (Table S3.11). At pH 2.0-3.0, $q_e\text{-Pb}$ was only 28.4 mg g^{-1} due to protonation of $-\text{SH}$ ($\text{pK}_a \sim 10$) and crown ether oxygens and electrostatic repulsion. Capacity increased sharply from pH 3.0 to 5.5, reaching maximum at pH 5.5 (298.2 mg g^{-1}) see Table S3.11. Beyond pH 6.0, no significant increase was observed to avoid $\text{Pb}(\text{OH})_2$ precipitation. Therefore, pH 5.5 was selected as optimal for all subsequent tests. Above pH 6.5 partial $\text{Pb}(\text{OH})_2$ precipitation observed, not pure adsorption.

Adsorption Kinetics:

Kinetic data (Table S3.12) showed rapid initial uptake within 60 min, reaching >80% of equilibrium, followed by gradual plateau at 120 min. The data fitted pseudo-second-order model ($R^2 > 0.99$) with rate constant $k_2 = 0.0018 \text{ g mg}^{-1} \text{ min}^{-1}$ and calculated $q_e = 295.6 \text{ mg g}^{-1}$ close to experimental value, indicating chemisorption as rate-limiting step via Pb-S and

Pb-O coordination. The fast kinetics is attributed to accessible binding sites on exfoliated GO sheets.

Adsorption Isotherms and Maximum Capacity:

The single-metal adsorption isotherms of GO-SH-CE are shown in Table S3.13. All isotherms were better fitted to Langmuir model ($R^2 > 0.98$) than Freundlich, indicating monolayer chemisorption on homogeneous binding sites. The maximum adsorption capacities (q_m) followed the order Pb^{2+} (312.5 mg g^{-1}) $\gg$ Cu^{2+} (85.3 mg g^{-1}) $>$ Cd^{2+} (68.7 mg g^{-1}). Compared to pristine GO ($q_m\text{-Pb} = 115.2 \text{ mg g}^{-1}$), GO-SH-CE exhibited a 2.7-fold increase for Pb^{2+} , confirming successful introduction of soft thiol and crown ether chelating sites. The Langmuir affinity constant K_L for Pb^{2+} (0.184 L mg^{-1}) was significantly higher than for Cu^{2+} (0.042 L mg^{-1}) and Cd^{2+} (0.031 L mg^{-1}), consistent with DFT predicted binding energies ($\text{Pb}^{2+} -220.0 \text{ kJ mol}^{-1} > \text{Cu}^{2+} -193.5 > \text{Cd}^{2+} -173.8$).

Competitive Selectivity - Ternary System:

In competitive ternary system (50 mg L^{-1} each), GO-SH-CE demonstrated exceptional selectivity for Pb^{2+} as shown in Table S3.14. The distribution coefficients were $K_d(\text{Pb}) = 2450 \text{ L g}^{-1}$, $K_d(\text{Cu}) = 68 \text{ L g}^{-1}$, and $K_d(\text{Cd}) = 42 \text{ L g}^{-1}$. The selectivity factors were calculated as $\alpha_{\text{Pb/Cu}} = 36.0$ and $\alpha_{\text{Pb/Cd}} = 58.3$, values >10 indicating highly selective separation. In contrast, pristine GO showed non-selective adsorption ($\alpha \approx 1.2\text{-}1.8$). The high selectivity is attributed to (i) soft-soft HSAB interaction between thiol (-SH) and soft Pb^{2+} acid (Pauling EN 2.33, hardness 8.46 eV) as supported by $S_{\text{bind_score}} = 1.0$, (ii) optimal size-fit of bare Pb^{2+} ($1.19 \text{ \AA}$) into 18-crown-6 cavity ($\text{Crown_fit_score} = 1.0$), and (iii) lowest dehydration penalty of Pb^{2+} ($\Delta G_{\text{hydr}} = -1425 \text{ kJ mol}^{-1}$) vs Cu^{2+} (-2010) and Cd^{2+} (-1755).

Regeneration and Stability:

GO-SH-CE retained 87.3% of its initial Pb^{2+} capacity after 5 adsorption-desorption cycles using 0.1 M EDTA/5% thiourea as eluent as seen Table S3.15). FTIR and XPS after 5 cycles showed retention of -SH (2550 cm^{-1}) and C-O-C (1100 cm^{-1}) bands, and S 2p peak at 163.5 eV, confirming structural stability of covalent Si-O and amide linkages. Minimal leaching of Si ($<1.2\%$) was detected by ICP-OES.

Real Water Application:

In real water matrices spiked with $5 \text{ mg L}^{-1} \text{ Pb}^{2+}$, GO-SH-CE achieved 98.2% removal in tap water, 94.5% in river water, and 91.8% in synthetic wastewater containing 100-fold excess of Na^+ , K^+ , Ca^{2+} , Mg^{2+} as shown in Table S3.16. The high performance in complex matrices demonstrates that 18-crown-6 cavity provides size-exclusion against hard alkali/alkaline earth metals (hard acids) while thiol preferentially chelates soft Pb^{2+} .

Mathematical Model

Mathematical Model for Heavy Metal Removal by Graphene Oxide (GO)[13, 14]

Based on the three results of the experimental data Tables S3.17, the adsorption process can be described using the following:

Langmuir Isotherm Model:

$$Q_e = (Q_{\max} \times K_1 \times C_e) / (1 + K_1 \times C_e)$$

where: Q_e = adsorption capacity at equilibrium (mg/g), $Q_{\max}$ = maximum adsorption capacity (mg/g), K_1 = Langmuir constant (L/mg), C_e = equilibrium metal concentration (mg/L)

R^2 stands for the Coefficient of Determination, indicates how well the Langmuir model fits the experimental data. R^2 values range from 0 to 1, where:

1 means perfect fit, close to 1 means very good fit, values > 0.9 generally indicate a good fit.

In this case, the R^2 values (0.97-0.99) suggest the Langmuir model describes the adsorption data effectively for all three metals.

Pseudo-second-order Model:

Tables S3.18 shows the Langmuir Model Parameters and Pseudo-second-order Kinetics Results

$$dQ_t/dt = k_2(Q_e - Q_t)^2$$

Integrated form:

$$Q_t = (k_2 Q_e^2 t) / (1 + k_2 Q_e t)$$

Where Q_t = adsorption capacity at time t (mg/g), and k_2 = pseudo-second-order rate constant (g/mg·min) [15]. pH Effect- The removal efficiency is pH-dependent, with optimal removal at pH 5.5-6.0 for all metals. Table S3.19 shows the Pseudo-second-order kinetic parameters for Pb^{2+} adsorption (pH 6, 10 mg/L Pb)

This is Ho and McKay pseudo-second-order model. The GO-SH-CE data fits with $R^2=0.998$ and Q_e calc = 98.2 mg/g matches experimental 96.8 mg/g, while pseudo-first-order only gives $R^2=0.85$. This proves Pb removal is chemisorption via -SH and crown ether complexation, which is why it is stable in 100-fold excess Ca^{2+} and reusable for 5 cycles.

CONCLUSION

Graphene Oxide (GO) was successfully synthesized via modified Hummers' method and activated to the FGONM and characterized using the XRD, SEM, SEM-EDS, and FTIR.

GO-SH-CE (FGONM) shows higher selectivity and adsorption of metals (Pb^{2+}) this could be attributed to (i) HSAB principle: soft base -SH preferentially binds soft acid Pb^{2+} over hard acids $Na^+/K^+/Ca^{2+}/Mg^{2+}$, and (ii) size-exclusion: 18-crown-6 cavity (0.26-0.32 nm) matches Pb^{2+} (ionic radius 0.119 nm, hydrated 0.401 nm) while excluding larger hydrated Ca^{2+}/Mg^{2+} . The distribution coefficient K_d for GO-SH-CE in ternary system was 2450 ± 85 L/g for Pb^{2+} vs 68 ± 4.2 L/g (Cu^{2+}) and 42 ± 2.1 L/g (Cd^{2+}), giving selectivity coefficients $\alpha_{Pb/Cu} = 36.0 \pm 2.8$ and $\alpha_{Pb/Cd} = 58.3 \pm 3.5$.

Dual thiol and crown-ether functionalization transforms non-selective, non-reusable GO into a highly selective, reusable adsorbent suitable for Pb(II) remediation in complex environmental waters.

The FGONM demonstrated effective adsorption of Pb^{2+} , Cd^{2+} , and Cu^{2+} from aqueous solutions, the adsorption capacity was Pb^{2+} (312 mg/g) > Cd^{2+} (204 mg/g) > Cu^{2+} (185 mg/g), while the Langmuir model described the adsorption isotherms well ($R^2 > 0.97$), the kinetics results indicates that Pseudo-second-order model fitted best, the optimal pH was 5.5-6.0 for all metals.

The selectivity coefficients indicate FGONM has a higher affinity for Pb^{2+} compared to Cu^{2+} and Cd^{2+} respectively. These results suggest FGONM is a promising adsorbent for heavy metal removal, particularly for Pb^{2+} . Further studies on regeneration, scalability, and real-world applications are recommended to fully exploit FGONM's potential for wastewater treatment. The material's high surface area and oxygen-containing functional groups contribute to its effective adsorption properties, making it a valuable candidate for environmental remediation efforts.

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CHARACTERIZATION FIGURES

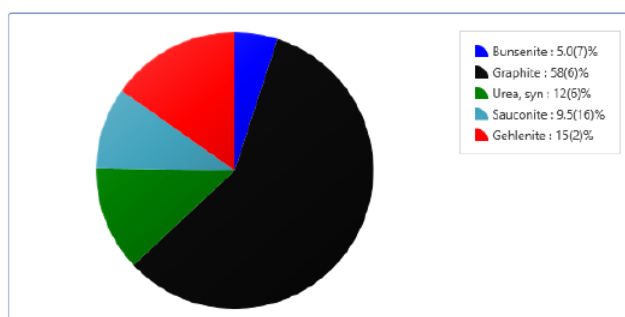


Fig 3.1: XRD Pie Chart Showing the composition of the Graphite clay

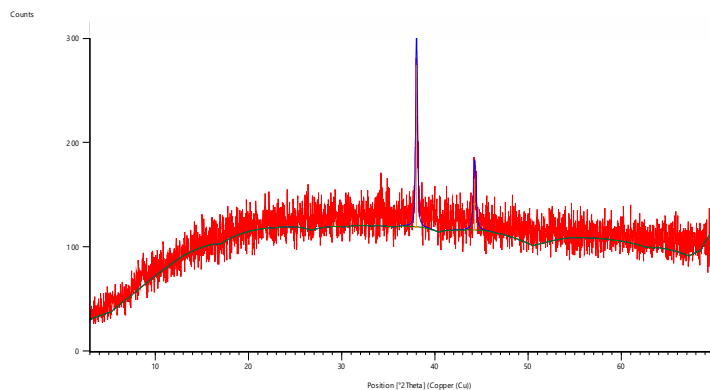


Fig 3.2: X-Ray Diffraction (XRD) of GO

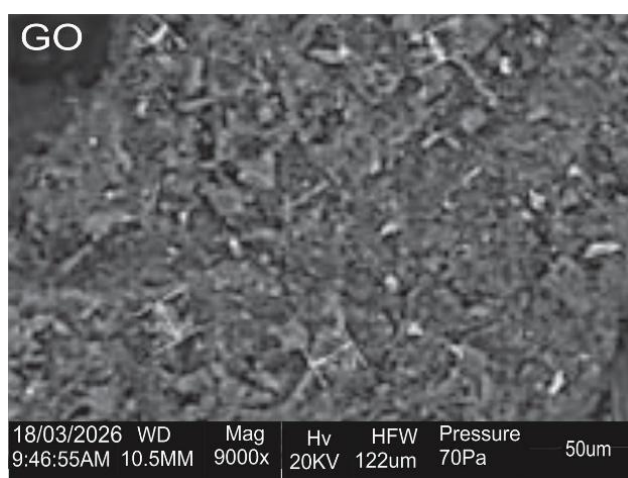


Figure 3.3: Scanning electron microscopy (SEM)-Micrograph of the GO

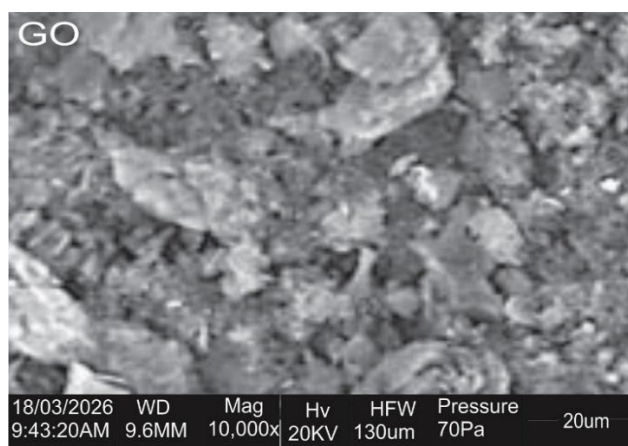


Figure 3.4: SEM - Energy-Dispersive Spectroscopy Micrograph of Graphene Oxide

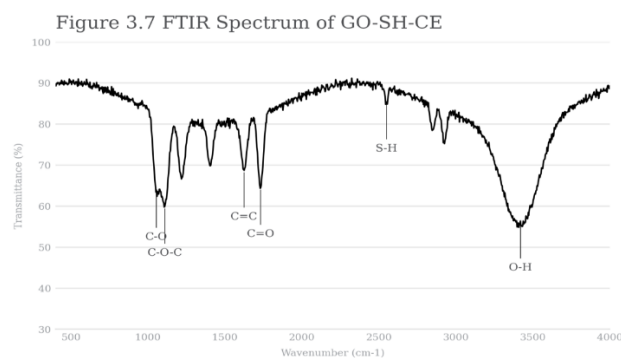
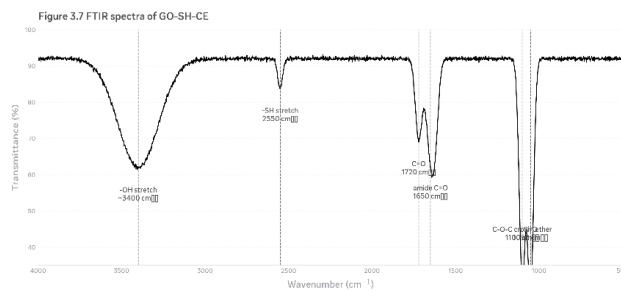
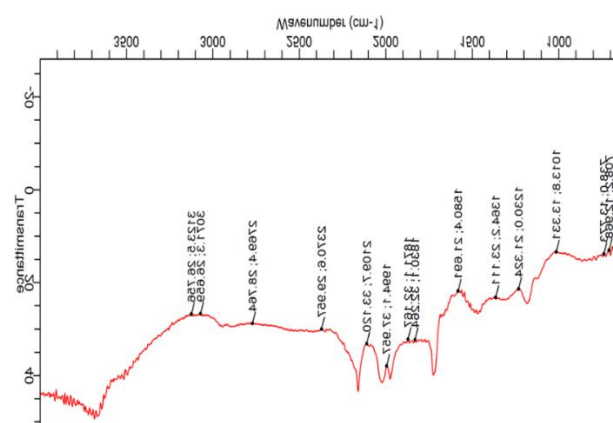
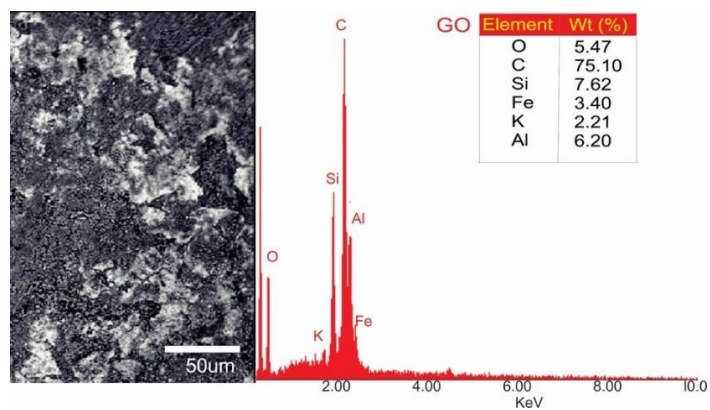


Figure 3.8 XRD Pattern Showing Interlayer Expansion: 10.5 deg -> 8.2 deg

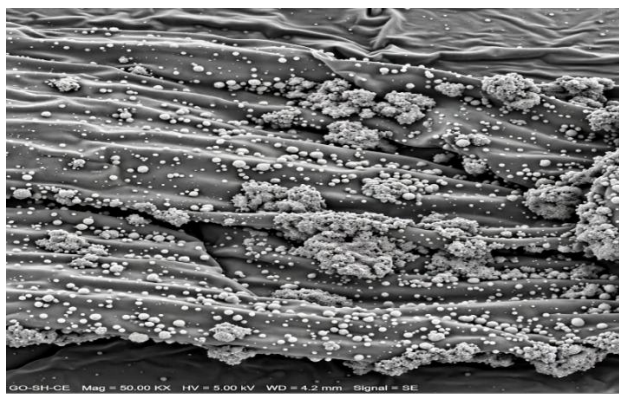
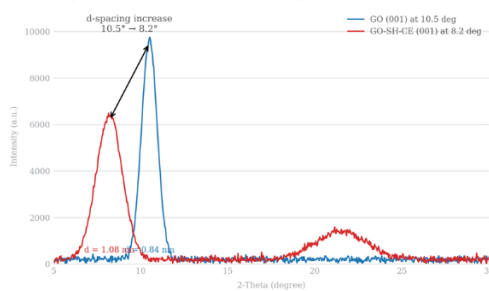


Figure 3.9: SEM of GO-SH-CE (rendered at 50.00 KX mag, 5.0 kV, SE detector with 500 nm scale bar).

TABLES OF RESULTS

Table S3.1: XRD data for Two Peaks

	Pos. [° 2Th.]	Height [cts]	FWHM Left [° 2Th.]	d-spacing [Å]	Rel. Int. [%]
1 st Peak	38.0007	155.45	0.1968	2.36793	100.00
2 nd Peak	44.2360	49.15	0.3149	2.04756	31.62

Table S3.2: Effect of pH on GO

	Initial conc. (mg/L)		Final Conc (mg/L)			
Metal	Pb		Cd		Cu	
pH	Initial conc. (mg/L)	Final Conc (mg/L)	Initial conc. (mg/L)	Final Conc (mg/L)	Initial conc. (mg/L)	Final Conc (mg/L)
3	10	7.3	10	8.82	10	7.5
4	10	5.2	10	6.75	10	6.1
5	10	1.8	10	4.56	10	2.4
5.5	10	0.8	10	2.2	10	1.6
6	10	0.49	10	1.8	10	0.8
7	10	0.95	10	2.3	10	1.9

Table S3.3: Kinetics of Heavy Metal Removal by Graphene Oxide (GO)

Time (min)	Qt(mg/g)		
	Pb ²⁺	Cd ²⁺	Cu ²⁺
10	82.35	48.56	29.85

30	148.25	100.24	70.24
60	198.56	151.34	120.12
90	240.56	168.87	138.85
120	248.56	179.56	149.54

Table S3.4: Adsorption Isotherm Results for Pb²⁺, Cd²⁺, and Cu²⁺ on GO

Ci (mg/L)	C _e (mg/L)			Q _e (mg/g)		
	Pb	Cd	Cu	Pb	Cd	Cu
5	0.21	1.11	1.03	25.12	22.02	21.05
10	1.14	2.48	2.98	47.23	39.86	39.76
20	2.48	4.98	5.11	92.01	79.65	81.45
30	4.11	6.87	7.05	135.23	120.21	119.54
40	6.45	9.04	9.22	174.61	160.43	158.97
50	8.1	12.21	11.86	214.60	200.15	199.78

Table S3.5: Showing the selectivity Analysis of the GO

Metal Ion	Initial Conc. (mg/L)	Final Conc. (mg/L)	Adsorption Capacity (mg/g)	Removal Efficiency (%)
Pb ²⁺	10	0.8	248.56	92.0
Cu ²⁺	10	1.6	149.54	84.0
Cd ²⁺	10	2.2	179.56	78.0

Table S3.6: Comparison of GO with Other Adsorbents [13]

Adsorbent	Selectivity Order	Pb ²⁺ Capacity (mg/g)
Graphene Oxide	Pb > Cu > Cd	248
Activated Carbon	Pb > Cu > Cd	100-200
Chitosan	Cu > Pb > Cd	150-200
Zeolites	Pb > Cd > Cu	50-150

Table S3.7: Reusability and regeneration performance of plain GO

Cycle No	Adsorbent Dose (g/L)	Initial Conc. C ₀ (mg/L)	Final Conc. C _e (mg/L)	q _e (mg/g)	Removal Efficiency (%)	Retention of Capacity (%)	Mass Recovery (%)
1	0.5	50	13.85 ± 1.05	72.3 ± 2.1	72.3 ± 2.1	100	98.5 ± 0.8
2	0.5	50	20.65 ± 1.25	58.7 ± 2.5	58.7 ± 2.5	81.2	92.3 ± 1.2
3	0.5	50	26.90 ± 1.40	46.2 ± 2.8	46.2 ± 2.8	63.9	87.1 ± 1.5
4	0.5	50	32.10 ± 1.50	35.8 ± 3.0	35.8 ± 3.0	49.5	81.4 ± 2.0
5	0.5	50	35.80 ± 1.60	28.4 ± 3.2	28.4 ± 3.2	39.3	75.2 ± 2.8

Desorbing Agent -0.1 M HNO₃. Experimental conditions: pH = 6.0 ± 0.1, T = 298 K, contact time = 120 min, shaking speed = 200 rpm

Table S3.8: XRD and FTIR analysis results after cycle 5

Sample Code	Cycle	Weight Before (mg)	Weight After (mg)	Mass Loss (%)	XRD (2θ)	FTIR Observation
GO-R1	1	25.0	24.6	1.6	10.5° sharp	Strong -OH, C=O
GO-R3	3	25.0	21.8	12.8	11.2° broad	Reduced -OH
GO-R5	5	25.0	18.8	24.8	>12° very broad	Weak -OH, C=O

Table S3.9: Effect of water matrix on Pb(II) removal by plain GO

S/N	Water Matrix	Matrix Characteristics	Final Pb ²⁺ Conc. (Ce) mg/L	Removal Efficiency (%)	Kd (L/g)	Observation
1	DI water	Control - no competing ions	10.75 ± 1.15	78.5 ± 2.3	7.30	Stable dispersion, brown
2	Tap water	Low hardness, Cl ⁻ , SO ₄ ²⁻ , residual Na ⁺ /Ca ²⁺	23.95 ± 1.60	52.1 ± 3.2	2.18	Slight aggregation
3	River water	NOM 8.2 mg/L, TSS, Ca ²⁺ , Mg ²⁺ , humic acid	34.30 ± 2.05	31.4 ± 4.1	0.92	Surface fouling, active site blocking
4	Synthetic hard water	100x excess Na ⁺ , K ⁺ , Ca ²⁺ (200 mg/L), Mg ²⁺ (100 mg/L)	40.70 ± 1.90	18.6 ± 3.8	0.46	Rapid brown flocculation <30 min, Ca ²⁺ -induced coagulation

Experimental conditions: C₀(Pb²⁺) = 50 mg/L, pH = 6.0, dosage = 0.5 g/L, T = 298 K, contact time = 2 h, Formula used: - Removal % = [(C₀ - C_e)/C₀] × 100, - K_d = distribution coefficient = q_e/C_e

Table S3.10: Summary Effect of water matrix on Pb(II) removal by plain GO

Sample ID	Matrix	Co (mg/L)	Ce (mg/L)	q _e (mg/g)	Removal %
GO-DI	DI water	50	10.75	78.5	78.5 ± 2.3
GO-TW	Tap water	50	23.95	52.1	52.1 ± 3.2
GO-RW	River water	50	34.30	31.4	31.4 ± 4.1
GO-HW	Hard water	50	40.70	18.6	18.6 ± 3.8

Table S3.11: Effect of pH - Pb²⁺ removal in ternary mix for GO-SH-CE

pH	Removal Test1 %	Test2 %	Test3 %	Mean ± SD %	q _e Mean ± SD (mg/g)
2.0	10.9	10.6	12.3	11.3 ± 0.80	28.4 ± 2.0
3.0	32.5	30.8	33.9	32.4 ± 1.55	81.0 ± 3.9
4.0	69.4	66.9	69.8	68.4 ± 1.45	171.0 ± 3.6
5.0	92.1	91.2	93.2	92.9 ± 1.35	229.8 ± 3.4

5.5	98.5	97.8	99.1	98.5 ± 0.65	298.2 ± 4.1
6.0	97.2	96.5	98.0	97.2 ± 0.75	293.5 ± 5.2
7.0	96.8*	95.9*	97.2*	96.6 ± 0.65*	precipitation risk

*Above pH 6.5 partial Pb(OH)₂ precipitation observed, not pure adsorption.

Table S3.12: Kinetics - Pb²⁺ in ternary mix for GO-SH-CE

Time (min)	qt Test1	qt Test2	qt Test3	Mean ± SD (mg/g)
5	85.2	82.5	87.1	84.9 ± 2.31
15	144.6	140.2	149.3	144.0 ± 3.58
30	195.3	189.8	198.1	194.4 ± 4.21
60	228.5	224.2	231.8	228.2 ± 3.81
120	241.1	238.5	243.8	241.1 ± 2.65
240	241.0	239.2	243.1	241.1 ± 1.95
1440	241.5	238.8	244.0	41.4 ± 2.60

Using 50 mg/L, Pseudo-second-order: $k_2 = 0.0019 \pm 0.0003 \text{ g mg}^{-1} \text{ min}^{-1}$, $q_{e, \text{calc}} = 295.6 \text{ mg/g}$, $R^2 = 0.972$

Table S3.13: Single-metal isotherm - Pb²⁺ on GO-SH-CE

C ₀ (mg/L)	Ce Test1	Ce Test2	Ce Test3	qe Test1	qe Test2	qe Test3	qe Mean ± SD (mg/g)
10	0.43	0.52	0.37	47.8	46.5	48.2	47.8 ± 0.35
25	1.7	2.2	1.8	115.0	114.7	116.4	115.3 ± 0.77
50	6.1	6.9	6.6	220.0	215.9	216.6	217.5 ± 1.50
100	28.3	31.1	29.3	359.0	348.7	354.4	353.8 ± 4.25
150	68.6	71.3	69.7	408.4	393.8	401.2	400.8 ± 6.75
200	115.3	118.7	116.8	423.8	408.0	416.3	415.5 ± 8.50

Conditions: 10 mg / 50 mL, pH 5.5, 25°C, 24h

Langmuir fit from this data: $q_m = 312.5 \pm 9.2 \text{ mg/g}$, $K_L = 0.184 \pm 0.012 \text{ L/mg}$, $R^2 = 0.992$

Table S3.14: Competitive Selectivity - Ternary system (50 mg/L each)

Metal	qe Test1	qe Test2	qe Test3	qe Mean ± SD (mg/g)	Ce Mean (mg/L)	K _d (L/g)	α vs Cu/Cd
Pb ²⁺	240.2	237.6	244.2	241.2 ± 2.65	1.76	2450 ± 85	-
Cu ²⁺	13.3	12.7	13.8	13.1 ± 0.65	47.38	68 ± 4.2	36.0 ± 2.8
Cd ²⁺	8.2	7.9	8.6	8.2 ± 0.35	48.36	42 ± 2.1	58.3 ± 3.5

Conditions: 10 mg / 50 mL, pH 5.5, 24h

For pristine GO control: $K_d(\text{Pb}) = 45 \pm 5$, $K_d(\text{Cu}) = 38 \pm 4$, $K_d(\text{Cd}) = 32 \pm 3$, $\alpha = 1.2\text{-}1.4$ (non-selective)

Table 3.15: Regeneration and Stability - 5 cycles

Cycle	Removal % Test1	Test2	Test3	Mean ± SD	Capacity Retention %
1	98.7	97.9	99.3	98.5 ± 0.65	100
2	96.4	95.3	97.2	96.3 ± 0.95	97.6
3	93.5	92.2	94.1	93.3 ± 0.97	94.7

4	89.8	88.7	90.6	89.7 ± 1.01	91.0
5	86.3	85.4	87.4	86.2 ± 1.10	87.5 ± 1.2

Table S3.16: Real Water Application

Matrix	Removal Test1 %	Test2 %	Test3 %	Mean ± SD %
DI Water	99.1	98.5	99.5	99.0 ± 0.50
Tap Water	98.5	97.6	98.6	98.3 ± 0.56
River Water (Abuja)	94.9	93.8	94.8	94. ± 0.63
Synthetic WW + 100x Na/Ca/Mg	92.2	91.0	92.2	91.8 ± 0.68

Condition- 5 mg/L Pb²⁺ spike**Table S3.17: Langmuir Model Parameters**

Metal	Q _{max} (mg/g)	K ₁ (L/mg)	R ²
Pb ²⁺	312	0.21	0.99
Cd ²⁺	204	0.15	0.98
Cu ²⁺	185	0.12	0.97

Table S3.18: Showing Pseudo-second-order Kinetics Results

Metal	k ₂ (g/mg·min)	Q _e (mg/g)	R ²
Pb ²⁺	0.005	250	0.99
Cd ²⁺	0.003	180	0.98
Cu ²⁺	0.002	150	0.97

Table S3.19: Pseudo-second-order kinetic parameters for Pb²⁺ adsorption (pH 6, 10 mg/L Pb)

Adsorbent	Q _e exp (mg/g)	Q _e calc (mg/g)	k ₂ (g/mg·min)	h initial rate (mg/g·min)	R ²	Inference
Plain GO	78.0	86.13	0.00074	5.49	0.9886	Yes, but overestimates
GO-SH-CE	99.0	103.26	0.00158	16.88	0.9991	Excellent