Coal Fly Ash Decorated with Graphene Oxide–Tungsten Oxide Nanocomposite for Rapid Removal of Pb\textsuperscript{2+} Ions and Reuse of Spent Adsorbent for Photocatalytic Degradation of Acetaminophen

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ABSTRACT: Coal fly ash was decorated with a graphene oxide–tungsten oxide nanorods nanocomposite (CFA/GO/WO\textsubscript{3}NRs nanocomposite) via a hydrothermal method and applied for the remediation of lead (Pb\textsuperscript{2+}) ions. The Pb\textsuperscript{2+} ion-loaded spent adsorbent (CFA/GO/WO\textsubscript{3}NRs + Pb\textsuperscript{2+} nanocomposite) was reused for the photodegradation of acetaminophen. CFA/GO/WO\textsubscript{3}NRs + Pb\textsuperscript{2+} nanocomposite displayed rapid removal of Pb\textsuperscript{2+} ions. Pseudo-second-order kinetics and the Langmuir isotherm model described the adsorption data. The adsorption capacity of the CFA/GO/WO\textsubscript{3}NRs nanocomposite was 41.51 mg/g for the removal of Pb\textsuperscript{2+} ions. Additionally, the Pb\textsuperscript{2+} ion-loaded spent adsorbent significantly influenced the degradation of acetaminophen by photocatalysis where 93% degradation was observed. It is worthy to note the reuse application of Pb\textsuperscript{2+} ion-loaded spent adsorbent as a photocatalyst, which will significantly reduce the secondary waste obtained from conventional adsorption methods.

1. INTRODUCTION

The increase in industrial activities and the high demand for medication have resulted in an uncontrollable release of heavy metals and toxic organic compounds into the aquatic environment, thereby causing water pollution. This environmental pollution is mainly due to human activities such as indiscriminate waste disposal including medical wastes, indiscriminate disposal of expired drugs, agricultural activities, smelting, mining, and storage batteries and electronics manufacturing, mainly in developing countries.\textsuperscript{1,2} Heavy metals which include lead, cadmium, and chromium cannot undergo biodegradation and consequently can last in water for decades. Among them, lead is commonly disposed into the environment by the manufacture of batteries, glass, ceramics, pigments, and paints.\textsuperscript{3} The concentration of lead accumulates in the environment with increasing hazardous effects because of continuous use and its nonbiodegradable nature. Health problems associated with long-time exposure to lead are anemia, increased blood pressure, memory loss, fatigue, and acute kidney and brain damage in both children and adults resulting in death.\textsuperscript{4} The World Health Organization (WHO) has therefore restricted the maximum permissible concentration of lead in drinking water as 10 μg/L.\textsuperscript{5}

Acetaminophen also known as paracetamol is among the active substances in most pharmaceuticals and applied as anti-inflammatory and analgesic medication for humans and animals. It is widely present in the environment and accumulates easily in water bodies. Acetaminophen has been identified in surface waters and wastewater as well as in drinking water.\textsuperscript{6} It has been reported that 58 to 68% of acetaminophen is released from the human body after therapeutic application and can lead to liver failure and death when used in excess.\textsuperscript{7} Therefore, cost-effective and efficient methods are needed to remove Pb\textsuperscript{2+} ions and acetaminophen from water and different industrial effluents.

Several methods have been historically utilized for the removal of lead ions from wastewater to ensure safe water consumption. The highly recommended technique for lead removal among other techniques is adsorption because of its simplicity, cost effectiveness, and efficiency.\textsuperscript{8} However, adsorption is faced with the challenge of secondary waste generation because of its simplicity, cost effectiveness, and efficiency.\textsuperscript{9} Acetaminophen is also released into the environment from various sources such as hospitals, households, and industries.\textsuperscript{10–12} Researchers are fabricating nanomaterials from different waste products, which are economical, effective, and efficient for heavy metal adsorption and photodegradation of organic pollutants.\textsuperscript{12}
Photocatalysis is a commonly used advanced oxidation technique in the degradation of toxic and refractory organic compounds, which include pharmaceuticals, dyes from textile industries, and pesticides. This is because of its capability to generate strong reactive radicals, specifically hydroxyl radicals, which can mineralize an extensive range of organic pollutants available in wastewater. Some metal-oxide semiconductors have proven to be outstanding photocatalysts. The semiconductors that are widely used as photocatalysts include WO$_3$, TiO$_2$, Cd$_2$O, and ZnO. Among these semiconductors, WO$_3$ is exceptional because of its small band gap of 2.8 eV, which can absorb visible light and degrade organic pollutants efficiently.

Coal fly ash (CFA), a waste which is generated from the combustion of coal at power plants, has been extensively used in the adsorption of heavy metals because of its features such as high morphology, affordability, availability, physical stability, and chemical properties (iron oxide, titanium dioxide, aluminum oxide, silicon dioxide, etc.). Consequently, CFA has its uses in solving the environmental problem of waste management and deterioration in the quality of water. However, its major drawback is its low adsorption capacity, which has limited its wide use in wastewater treatment. CFA has been modified with carbon materials to enhance its surface area, incorporate robust functional groups, and increase the adsorption capacity through different methods including hydrothermal treatment. For instance, Umejuru et al., 2020 synthesized CFA/carbon hybrid nanocomposites using hydrothermal treatment techniques, and these materials were applied in heavy metal adsorption and reported a high sorption capacity. Graphene is one of the carbon materials that has been extensively used as a nanocomposite, including graphene oxide (GO), because of its ability in the adsorption of heavy metals and degradation of organic pollutants in wastewater. This is due to its outstanding properties such as robust surface functional groups, large surface area, good adsorption capability, very good electrical features, and thermal and mechanical stabilities. GO is obtained from graphite via improved methods, and it has been used and established as a nanocomposite. The carbon-based composite adsorbents have lower adsorption capacity for the removal of heavy metals from wastewater samples. The incorporation of WO$_3$ nanoparticles into carbon-based composites to form nanocomposites can increase its adsorption capacity and strength.

2. RESULTS AND DISCUSSION

2.1. Formation of CFA/GO/WO$_3$NRs Nanocomposite. The CFA contained mainly Si, Al, Fe, and O in which Si is involved in the formation of the composite with GO. GO interacted effectively with CFA because of hydrogen bonding between OH, COOH groups of GO, and Si−O of CFA. The effective binding of CFA/GO with negatively charged surfaces has a strong tendency to interact with WO$_3$NRs, thereby leading to the successful fabrication of CFA/GO/WO$_3$NRs nanocomposite. It shows a highly negatively charged surface, which was confirmed by the zeta potential analysis. This adsorbent was therefore suitable for efficient removal of Pb$^{2+}$ ions from aqueous solution.

2.2. Characterization. 2.2.1. X-ray Diffraction Analysis. Figure 1Aa shows that the crystals in CFA are mainly diffracted at peaks at $2\theta = 16.5, 20.73, 27.3, 33.50, 41.05, 60.89$, and $50.03^\circ$, which are associated with quartz, mullite, hematite, and magnetite. Figure 1Ab shows that more intense peaks appeared at $2\theta = 12.70^\circ (100), 27.82^\circ (101), 28.30^\circ (200), 32.53^\circ (202), 35.35^\circ (111), 46.38^\circ (201), 64.70^\circ (622), 78.38^\circ (414)$, and $80.92^\circ (422)$, which corresponded to the amorphous nature of GO to form the CFA/GO/WO$_3$ nanocomposite. In addition, a small broad peak was observed at around $2\theta = 16.56^\circ$, which corresponds to the amorphous nature of GO to form the CFA/GO/WO$_3$ nanocomposite [shown with the highlighted red circle with the expanded spectrum as shown in Figure 1Ab (inset)]. This data confirmed the formation of the CFA/GO/WO$_3$NRs nanocomposite. The successful incorporation of WO$_3$NRs on CFA/GO resulted in enhanced adsorption of Pb$^{2+}$ ions.

Figure 1. (A) XRD patterns of (a) CFA, (b) CFA/GO/WO$_3$NRs nanocomposite, and (c) CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite, (B) FTIR spectra for GO, and (C) FTIR for (a) CFA, (b) CFA/GO/ WO$_3$NRs nanocomposite, and (c) CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite.
Figure 2. A (a,b) TGA and DTA of CFA/GO/WO₃NRs nanocomposite and (B) surface area of (a) CFA and (b) CFA/GO/WO₃NRs nanocomposite.

Figure 3. SEM of CFA (a) and CFA/GO/WO₃NRs nanocomposite of (b) 20 μm, (c) 10 μm, and after adsorption (d). Energy-dispersive X-ray analysis of CFA (e), CFA/GO/WO₃NRs nanocomposite (f), and after adsorption (g).
adsorbent (CFA/GO/WO3NRs + Pb2+ nanocomposite) revealed that most of the peaks became less intense and disappeared after Pb2+ ion adsorption as shown in Figure 1Ac. This was due to the strong binding interaction between the negatively charged surface of the CFA/GO/WO3NRs nanocomposite and the positively charged Pb2+ ions.25

2.2.2. Fourier Transform Infrared Study. The Fourier transform infrared (FTIR) spectrum of GO, as presented in Figure 1B, reveals different peaks corresponding to several functional groups containing carboxylic, hydroxyl, and oxygen groups, which confirms the successful formation of GO. The peak exhibited at 3361 cm−1 is attributed to the stretching vibration of the O–H group. The peak at 1714 cm−1 is due to the C==O stretching vibration of the carboxylic acid (COOH) functional group. The peak at 1418 cm−1 was assigned to the C–C stretching vibration of the aromatics group. Peaks appeared at 1023 cm−1 as a result of C–H stretching in the aliphatic groups and at 872 cm−1 due to the ==C–H bend (alkenes functional group).26 The abovementioned vibration peaks all confirm the successful formation of GO from graphite powder by modifying a reported method for its synthesis.27

CFA showed various peaks in Figure 1Ca. The low-intensity peak observed at 3416 cm−1 was attributed to the O–H groups of the water molecules on CFA. The peaks at 1393 and 1086 cm−1 were assigned to the asymmetric and symmetric stretching vibrations of Si–O–Al groups in CFA. These vibrations also provided evidence of the amorphous nature of SiO2.28,29 The peak 1639 cm−1 was assigned to the bending vibration of the O–H bond due to a water molecule in CFA.30 At 559 cm−1, the bending vibration confirmed the presence of the Si–O–Si bond in CFA as shown in Figure 1Ca.

Figure 1Cb reveals various functional groups in the synthesized CFA/GO/WO3NRs nanocomposite. The large peak in the range of 3060–3587 cm−1 confirmed the O–H stretching vibration of functional groups and the presence of water molecules.31 The peaks at 1400 and 1052 cm−1 indicate the C–C stretching vibration in aromatics and the C–H stretch vibration of aliphatic groups. A small sharp intensity peak was observed at 881 cm−1 because of the stretching vibration of the W–O–W bond of WO3NRs on the CFA/GO/WO3NRs nanocomposite.32 The band at 559 cm−1 was assigned to the stretching vibration of Si–O–Si. In summary, these various functional groups on the CFA/GO/WO3 nanocomposite surface facilitated the adsorption of Pb2+ ions by providing more adsorption sites. There was a reduction in the peak intensity as well as a shift in the peak position after Pb2+ ion adsorption as shown in Figure 1Cc. This was because of the interaction between Pb2+ ions and various functional groups on the CFA/GO/WO3NRs nanocomposite.

2.2.3. Thermal Analysis. Figure 2Aa,b shows the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results. The TGA results showed a weight loss of 4.7% between 21 and 120 °C. This resulted from the loss of humidity and adsorbed water. The large drop in mass in the range 170–429 °C (4.4%) resulted from the loss of volatile organic compounds (acetone and methanol etc.) on the CFA/GO/WO3NRs nanocomposite, and this weight loss indicates an exothermic reaction with the DTA curve (Figure 2Ab). The other loss in mass began from 500 to 678 °C (3.3%) because of the deformation of the metal oxide in the CFA/GO/WO3NRs nanocomposite.33,34 At above 700 °C, the TGA stability was achieved as indicated by the straight line. Thus, the CFA/GO/WO3NRs nanocomposite is a thermally stable material for wastewater applications.

2.2.4. Brunauer–Emmett–Teller Characterization. The specific surface area is an important parameter, which shows the textural characteristics of the adsorbent and was determined using the Brunauer–Emmett–Teller (BET) analysis method under nitrogen gas desorption–adsorption, 10 °C/min. The BET surface areas of the CFA and the CFA/GO/WO3NRs nanocomposite are shown in Figure 2Ba,b and showed the H3 loop model. The surface areas of both the CFA and the CFA/GO/WO3NRs nanocomposite were estimated as 6.0754 and 11.158 m2/g, respectively. The CFA/GO/WO3NRs nanocomposite promised higher surface area, more than 2-fold compared to CFA, which was favorable for the adsorption of Pb2+ ions.

2.2.5. Surface Morphology. The surface morphology of the CFA and the CFA/GO/WO3NRs nanocomposite (before and after adsorption) was investigated to confirm the transformation of materials. These images are shown in Figure 3a–d. The smooth spherical structures of CFA are evident in Figure 3a. The

Figure 4. TEM images at various magnifications before adsorption (A) 500, (B) 200, and (C) 100 nm and after adsorption (D) 200, (E) 100, and (F) 50 nm.
morphism of the CFA/GO/WO3NRs nanocomposite was investigated before (Figure 3b,c) and after adsorption (Figure 3d). Figure 3b shows the incorporation of GO and WO3NRs into CFA with images of small and large netlike balls at 20 μm, which contributed to the high removal of Pb2+ ions. It can be clearly observed that at 10 μm, spherical CFA was wrapped with GO and WO3NRs. Also GO formed a layer, and WO3NRs can be noticed as displayed in Figure 3c. There was not much difference in morphology after adsorption. This can evidently be noticed in Figure 3d suggesting the stability of the CFA/GO/WO3NRs nanocomposite. Investigation was conducted on the elemental composition of the CFA and the CFA/GO/WO3NRs nanocomposite (before and after adsorption) to confirm the elements present (Figure 3e−g). The major elements in the CFA are O, C, Si, Al, and Fe with minute percentages of other metal oxides, as shown in Figure 3e. The presence of WO3 can be noticed in Figure 3f, which confirms its successful incorporation into the nanocomposite. The presence of Pb2+ in (Figure 3g) is a confirmation of its adsorption.  

2.2.6. Transmission Electron Microscopy Characterization. Transmission electron microscopy (TEM) images of the CFA/GO/WO3NRs nanocomposite at magnifications 500, 200, and 100 nm are displayed in Figure 4A−D. Figure 4A shows the formation of several WO3 NRs observed on the GO/CFA cluster at magnification 500 nm. Figure 4B shows WO3NRs, which were clearly observed on GO/CFA at a high magnification of 200 nm with yellow arrows showing, GO, CFA, and WO3 NRs. Figure 4C shows the crystallinity of WO3 NRs which was recorded at a higher magnification of 100 nm. These results confirm the successful hybridization of WO3NRs on the CFA/GO nanocomposite, which was beneficial for the adsorption of Pb2+. This also aids in the transfer of charges for the photocatalytic activity of the spent adsorbent in the reuse application. The adsorption of Pb2+ ions in the CFA/GO/WO3NRs nanocomposite to give the spent adsorbent of CFA/GO/WO3NRs + Pb2+ nanocomposite was also investigated for size and morphology with TEM at various magnifications of 200, 100, and 50 nm as shown in Figure 4D−F. From the image Figure 4D−F, there were no significant changes in the morphology of the CFA/GO/WO3NRs nanocomposite after the adsorption of Pb2+ ions. This spent adsorbent was effectively applied in the degradation of acetaminophen by photocatalysis when exposed to visible light. This is because the electron−hole recombination rate was reduced.  

2.2.7. X-ray Photoelectron Spectroscopy Study. X-ray photoelectron spectroscopy (XPS) was performed to determine the surface elements and bonding interactions as well as to understand the adsorption mechanism before and after adsorption. Figures 5,6 display the XPS results obtained for the CFA/GO/WO3NRs nanocomposite (before adsorption)
and the CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite (after adsorption), respectively. The survey XPS spectrum appeared with various elements in the CFA/GO/WO$_3$NRs nanocomposite as shown in Figure 5Aa. The C 1s for the CFA/GO/WO$_3$ NRs nanocomposite displayed peaks at 281.93 and 284.90 eV corresponding to C−C and C=O bonds, respectively, as shown in Figure 5Ab. The O 1s of the CFA/GO/WO$_3$NRs nanocomposite at 528.92 eV assigned to W−O−N bond. The W 4d spectra of the CFA/GO/WO$_3$NRs nanocomposite show three peaks at 244.57, 257.07, and 267.62 eV associated with W4d$_{5/2}$ and W4d$_{3/2}$. The W 4f spectra of the CFA/GO/WO$_3$NRs nanocomposite display two peaks at 32.39 and 34.48 eV associated with 4f$_{7/2}$, as shown in Figure 5A(c). These confirm the successful incorporation of WO$_3$ into the CFA/GO/WO$_3$NRs nanocomposite, which favor the adsorption of Pb$^{2+}$ ions.

The XPS analysis after adsorption confirms the presence of Pb$^{2+}$ ions on the surface of the CFA/GO/WO$_3$NRs nanocomposite as shown in Figure 6. Figure 6a presents the XPS full-scan survey spectra after adsorption. The C 1s spectra after adsorption revealed two peaks at 281.98 and 284.69 eV. This indicates that the binding energy of C 1s spectra did not present remarkable changes after adsorption as shown in Figure 6b. Possibly, the interaction between Pb$^{2+}$ ions and carbon on the CFA/GO/WO$_3$NRs nanocomposite during the adsorption process was mainly because of weak chemical interactions or nonspecific interactions. The fitting curve of O 1s after adsorption displayed a peak at 529.13 eV, which corresponds to Pb−O. This indicates coordination between Pb$^{2+}$ ions and the oxygen atom present in the carbonyl group on the surface of the CFA/GO/WO$_3$NRs nanocomposite during adsorption as shown in Figure 6c. Additionally, the O 1s binding energy of the CFA/GO/WO$_3$NRs nanocomposite slightly shifted from 528.92 to 529.13 eV after adsorption. The fitting curve presented two peaks at 411.48 eV and 437.27 assigned to Pb 4d$_{5/2}$ and Pb 4d$_{3/2}$, respectively, as shown in Figure 6d. The W 4f spectra after adsorption showed four peaks at 244.48, 256.88 eV and 266.31 eV, which are associated with W4d$_{5/2}$ and W4d$_{3/2}$ (Figure 6e). This revealed that W 4f spectra experienced significant change after adsorption with the addition of new peaks. The W 4f spectra had a little shift after adsorption because of its interaction with Pb$^{2+}$ as shown in Figure 6f. The XPS spectra of Pb 5s + Pb 4f presented four peaks, one peak at 136.26 eV (Pb 4f$_{5/2}$), 141.34 eV (Pb 4f$_{7/2}$), 143.93 eV (Pb 4f$_{5/2}$), and 151.07 eV (Pb 5s) as presented in Figure 6g.

2.2.8. UV−Visible Diffuse Reflectance Study. UV−visible diffuse reflection spectroscopy (DRS) investigation was carried out to estimate the band gap energy of the CFA/GO/WO$_3$NRs nanocomposite (before adsorption) and the CFA/GO/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite (after adsorption), respectively. The survey XPS spectrum appeared with various elements in the CFA/GO/WO$_3$NRs nanocomposite as shown in Figure 5Aa. The C 1s for the CFA/GO/WO$_3$ NRs nanocomposite displayed peaks at 281.93 and 284.90 eV corresponding to C−C and C=O bonds, respectively, as shown in Figure 5Ab. Figure 5Ac shows a peak for O 1s of the CFA/GO/WO$_3$NRs nanocomposite at 528.92 eV assigned to a W−O−N bond. The W 4d spectra shown in Figure 5Ad display three peaks at 244.57, 257.07, and 267.62 eV associated with W4d$_{5/2}$ and W4d$_{3/2}$. The W 4f spectra of the CFA/GO/WO$_3$NRs nanocomposite display two peaks at 32.39 and 34.48 eV associated with 4f$_{7/2}$, as shown in Figure 5A(e). These confirm the successful incorporation of WO$_3$ into the CFA/GO/WO$_3$NRs nanocomposite, which favor the adsorption of Pb$^{2+}$ ions.

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WO₃NRs + Pb²⁺ nanocomposite (after adsorption) as presented in Figure 7Aa,b. The results indicated that peaks appeared at 297 and 310 nm for the CFA/GO/WO₃NRs nanocomposite and the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite. This confirms that Pb²⁺ ions adsorbed on the CFA/GO/WO₃NRs nanocomposite significantly affected the CFA/GO/WO₃NRs nanocomposite for photocatalysis. The estimated band gap energy for the CFA/GO/WO₃NRs nanocomposite and the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite is 4.03 and 3.98 eV. These band gap energies which were calculated from the Tauc plot show the energy of light (hv, eV) versus (αhv)¹/² as shown in Figure 7Ba,b. The results showed that there was a decrease in the band gap energy after adsorption of Pb²⁺ ions, which favored photodegradation.

Figure 7. (A) DRS-UV spectra for the (a) CFA/GO/WO₃NRs nanocomposite and (b) CFA/GO/WO₃NRs + Pb²⁺ nanocomposite. (B) Tauc plot for the (a) CFA/GO/WO₃NRs nanocomposite and (b) CFA/GO/WO₃NRs + Pb²⁺ nanocomposite. (C) FL spectra for the (a) CFA/GO/WO₃NRs nanocomposite and (b) CFA/GO/WO₃NRs + Pb²⁺ nanocomposite.

Figure 8. Effect of different parameters. (A) Adsorbent dosage (Pb²⁺ ions 200 mg/L, dosages of 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, and 0.3 g, 200 rpm, T = 25 °C), (B) pH (2 to 8, dosage = 0.04 g/L, T = 25 °C, Pb²⁺ ions = 200 mg/L), and (C) zeta potential.
nm. The emission peak at 345 nm was recorded in the FL spectrum of CFA/GO/WO3NRs because of oxygen vacancy or defects in WO3 NRs and reported.42 Figure 6Cb shows that the FL intensity decreased at 355 nm with an excitation of 290 nm for CFA/GO/WO3NRs + Pb2+ nanocomposite because of minimized electron–hole recombination rate, high charge separation, and reactive species hydroxyl radicals and oxygen radicals for photocatalytic degradation of acetaminophen under visible light irradiation.43

2.3. Batch Adsorption. 2.3.1. Dosage Effect. To investigate the optimal dosage for the Pb2+ ions (30 mL) while maintaining the initial concentration fixed at 200 mg/L, different dosages (0.02, 0.04, 0.06, 0.08, 0.1, 0.2, and 0.3 g) of the CFA/GO/WO3NRs nanocomposite material were added. Figure 8A presents the results of the experiments. It can be noted that the percentage removal increased from 71 to 99% as the CFA/GO/WO3NRs nanocomposite dosage increased from 0.02 to 0.04 g. The increasing of adsorbent dosage resulted in more available adsorption sites, which in turn increased the Pb2+ ion removal percentage. Further increase of adsorbent dosage (0.06, 0.08, and 0.1 g) caused a slight and steady decrease of 98% in the removal percentage. In addition, at dosages of 0.2 and 0.3 g, the removal percentage reduced to 97 and 96%. This result suggests that an increase in the dosage and agglomeration of the adsorbent could lead to the prevention of Pb2+ ions from accessing the adsorption sites. Similarly, this pattern has been reported for adsorption of Pb2+ ions by other researchers.2,3,4,44

2.3.2. Effect of pH on Removal of Pb2+ Ions. The effect of pH is one of the critical parameters that significantly affects the removal of heavy metal ions by adsorption. This effect was studied over the pH range of 2 to 8 as shown in Figure 8B. The percentage removal increases with increasing pH and became constant between pH 4.6 and 8. The results indicate that pH has a considerable effect on Pb2+ ion adsorption onto the CFA/GO/WO3NRs nanocomposite. The concentration of H+ ions decreases rapidly with an increase in pH due to lesser competition between the H+ ions and Pb2+ ions for the adsorption sites. This leads to an increase in Pb2+ ion adsorption because of a higher affinity for the active centers of the WO3 NRs (W=O bond), GO (COOH, OH and O), and CFA particles. This is due to the presence of charged oxides of SiO2, Al2O3, Fe2O3, and TiO2.4,5,6 The mechanism of ion exchange between H+ and Pb2+ ions is described by equations as shown below

\[
\text{AOH} + H_2O^+ \rightarrow AOH_2^+ + H_2O \quad (1)
\]

\[
\text{AOH} + OH^- \rightarrow A^- + H_2O \quad (2)
\]

\[
2(AO^-) + Pb^{2+} \rightarrow (AO)_2 Pb \quad (3)
\]

where A could be W, GO, Si, Fe, or Al. As the pH increases, the amount of AO− ions on the CFA/GO/WO3NRs nanocomposite surface increased, thereby resulting in increased electrostatic attraction between the ions and the adsorbent.4,44

2.3.3. Zeta Potential. Zeta potential analysis is useful in determining the point of zero charge of the adsorbent. The zeta Potential for the CFA/GO/WO3NRs nanocomposite was investigated in the pH range of 2 to 10 and presented in Figure 8C. The CFA/GO/WO3NRs nanocomposite surface charge was found to be negatively charged between −1.27 and 40.8 mV. This can be attributed to the deprotonation of the functional groups (oxygen, carboxylic, and hydroxyl) available on the surface of WO3 NRs, GO, and CFA.4,44 There is a steady increase in the negative charge as the pH increases. From the data, the CFA/GO/WO3NRs nanocomposite has negatively charged particles, which are favorable for the removal of Pb2+ ions.

2.3.4. Adsorption Isotherms. The evaluation of adsorption isotherms is a key factor because it helps to reveal the interaction that occurs between the adsorbent and the adsorbate. Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models were applied in their linear forms (eqs 8, 9 and 10). The Langmuir model is associated with monolayer adsorption, whereas the Freundlich model represents a multilayer adsorption system. The D–R model is widely applied in the determination of the nature of adsorption. The evaluation of isotherms was achieved by maintaining the temperature at 25, 35, and 45 °C while varying the Pb2+ ion initial concentrations between 50 and 300 mg/L using 0.04 g of CFA/GO/WO3NRs nanocomposite. Eq 10 presents the dimensionless separation factor (Rc) which provides information on the favorability of the adsorption process. The determination of the adsorption capacity of the CFA/GO/WO3NRs nanocomposite was carried out by investigating the adsorption thermodynamics of Pb2+ ions and the effect of temperature. The linear forms of the Langmuir, Freundlich and D–R isotherm models are shown in Figure 9A–C. Table 3 shows the estimated isotherm results for Pb2+ ion adsorption onto the CFA/GO/WO3NRs nanocomposite.

From the results (Figure 9A–C) and (Table 1), the Langmuir isotherm showed higher correlation coefficients when compared to Freundlich and D–R isotherms. This indicates that Pb2+ ion adsorption process was predominantly a monolayer adsorption without mutually interacting with the adsorbed molecules. It is further noted that the maximum adsorption capacity increased from 34.72 to 41.51 mg/g as the temperature increased from 25 to 45 °C. This implied an endothermic nature of Pb2+ ion adsorption onto the CFA/GO/WO3NRs nanocomposite. Langmuir equation

\[
\frac{C}{q} = \frac{1}{q_m b} + \frac{C}{q_m}
\]

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11162
Pb²⁺ Ion Removal from Aqueous Solution

Table 3. Thermodynamics for Pb²⁺ Ion Adsorption onto the CFA/GO/WO₃ Nanocomposite

| Parameters | Temperature (°C) | Langmuir | Freundlich |
|------------|------------------|----------|------------|
|             | 25               | 35       | 45         |
| qₑ₀ (mg/g) | 34.72            | 39.90    | 41.51      |
| R²         | 0.9819           | 0.9380   | 0.9952     |
| b (L/mg)   | 1.0000           | 1.002    | 1.0000     |
| Rₑ        | 0.0114           | 0.0114   | 0.0114     |

Freundlich

kₑ (mg/g) | 32.04          | 31.23    | 1.11       |

N | 26.04          | 15.43    | 9.57       |

R² | 0.0436         | 0.1496   | 0.2006     |

D–R

qₑ₀ (mg/g) | 1.30           | 1.34     | 1.33       |

E (kJ/mol) | 4.61 × 10⁻³     | 4.42 × 10⁻³ | 2.0 × 10⁻³ |

R² | 0.38096        | 0.48028  | 0.80732    |

Table 2. Comparison of Adsorption Capacity of the CFA/GO/WO₃ Nanocomposite with Other Adsorbents Used for Pb²⁺ Ion Removal from Aqueous Solution

| s. no | Adsorbents                      | Adsorption Capacity (mg/g) | Isotherms | Reference |
|-------|---------------------------------|-----------------------------|-----------|-----------|
| 1     | KPPa                            | 16.37                       | Langmuir  | 25        |
| 2     | MKPPb                           | 14.14                       | Langmuir  | 25        |
| 3     | fly ash from CFBC                | 51.98                       | Langmuir  | 34        |
| 4     | grafted-IIPd                    | 38.5                        | Langmuir  | 55        |
| 5     | RAFTP–IIIp                      | 53.8                        | Freundlich| 55        |
| 6     | silicate porous material         | 44.83                       | Freundlich| 56        |
| 7     | GO                              | 35.6                        | not stated| 57        |
| 8     | activated carbon                | 21.2                        | Freundlich| 58        |
| 9     | CFA/GO/WO₃NRs nanocomposite     | 41.51                       | Langmuir  | this study|

* Bauhinia purpurea (Kaniar) pod powder (KPP). b Magnetic Bauhinia purpurea (Kaniar) powders (MKPP). c Circulating fluidized bed combustion (CFBC). d Ion imprinted polymers (IIPs). e Reversible addition–fragmentation (RAFTP)–ion imprinted polymers (IIPs).

Table 3. Thermodynamics for Pb²⁺ Ion Adsorption onto the CFA/GO/WO₃ Nanocomposite

| Temperature (K) | ΔH° (kJ/mol) | ΔS° (kJ/mol) | ΔG° (kJ/mol) |
|-----------------|--------------|--------------|--------------|
| 298             | 38.22        | 0.1501       | -6.51        |
| 308             | -8.01        |              |              |
| 318             | -9.51        |              |              |

\[
E = \frac{1}{\sqrt{-2\beta}}
\]

\[C₀ \text{ (mg/L)} \text{ and } qₑ \text{ (mg/g)} \text{ represent the Pb}^{2+} \text{ ion concentration and the amount of Pb}^{2+} \text{ ions adsorbed at the equilibrium state; } qₘ \text{ and } b \text{ refers to the Langmuir constant associated with the maximum adsorption capacity and binding energy; } kₑ \text{ and } n \text{ are the Freundlich constant and adsorption intensity. } Rₑ \text{ is a key parameter related to the dimensionless Langmuir model separation factor, as stated in (eq 13), used to test the feasibility of the adsorption system. } β \text{ represents the D–R isotherm constant estimated from the slope obtained from the plot of } \ln qₑ \text{ against } e², \text{ and } ε \text{ is the Polanyi potential evaluated from eq 8 above. } R \text{ is the gas constant (0.008314 kJ/mol/K), } T \text{ is the temperature in Kelvin, and } E \text{ is the adsorption free energy associated with } β \text{ in eq 12 above.}
\]

\[
Rₑ = \frac{1}{1 + bC₀}
\]

where \(C₀ \text{ (mg/L)}\) refers to the initial Pb²⁺ concentration and \(b \text{ (L/mg)}\) is the Langmuir constant. The \(Rₑ\) ranging between 0 and 1 suggests a favorable adsorption system. The maximum adsorption capacity was compared with that of other adsorbents reported in the literature for Pb²⁺ ion adsorption (Table 2).

2.3.5. Thermodynamics. To gain further insight into the adsorption process, thermodynamics parameters of Gibbs free energy (\(ΔG°\)), enthalpy (\(ΔH°\)), and entropy (\(ΔS°\)) were applied using eqs 14 and 15

\[
ΔG = -RT \ln K_d = -RT \ln \left( \frac{m \cdot q}{Cₐ} \right)
\]

\[
\ln K_d = \ln \left( \frac{m \cdot q}{Cₐ} \right) = \frac{ΔS°}{R} = \frac{ΔH°}{RT}
\]

where \(K_d\) is the thermodynamic equilibrium constant, \(m \text{ (g L}^{-1})\) is the adsorbent dose, \(q₀/Cₐ\) is the adsorption affinity, \(R\) is the gas constant (0.008314 kJ/mol/K), and \(T\) is the temperature in Kelvin. The slope and intercept plot of \(\ln(mq/Cₐ)\) versus \(1/T\) gave the values of \(ΔH°\) and \(ΔS°\) as presented in Figure 9D. Table 3 shows the estimated thermodynamics parameters. It can be noticed from Table 3 that as the temperature increases, \(ΔG°\) becomes more negative, thus indicating a more spontaneous reaction, which is favorably affected by the temperature. The adsorption process was confirmed as endothermic when the value of \(ΔH°\) is positive as indicated in Table 3. The positive value of \(ΔS°\) suggested increased randomness during adsorption.

2.3.6. Effect of Contact Time and Adsorption Kinetics. This study was conducted in the time range of 10–70 min and temperature range of 25–45 °C using 0.04 g of the adsorbent with the initial Pb²⁺ concentration of 50 mg/L. The adsorption of Pb²⁺ was rapid at 40 min for 25 °C, 70 min for 35 °C, and 50 min for 45 °C. The results in Figure 10A showed an alternating increase and decrease for Pb²⁺ adsorbed. This suggests that the saturation of adsorption sites occurred to a maximum capacity and was attributed to the rapid adsorption of Pb²⁺ ions on the surface of the CFA/GO/WO₃ nanocomposite. After saturation time, the adsorption rate displayed the decrease and increase pattern, which may be due to the diffusion of Pb²⁺ ions into the pores of the nanocomposite.
onto the CFA/GO/WO3 nanocomposite. The high values of equilibrium and time shown in Figure 10C. Table 4 shows the results for kinetic and qe obtained for the correlation coefficient. The pseudo-second-order rate constant (Figure 10B) and qf versus 1/t for intraparticle diffusion as shown in Figure 10C. Table 4 shows the results for kinetic and intraparticle diffusion models evaluated for Pb2+ ion adsorption onto the CFA/GO/WO3 nanocomposite. The high values obtained for the correlation coefficient and the level of closeness between calculated qe values and the experimental qe values suggests that pseudo-second-order is highly suitable to describe the adsorption kinetic of Pb2+ ions onto the CFA/GO/WO3 nanocomposite.

In the intraparticle diffusion mode, qt is plotted against t^{0.5}. The intraparticle diffusion process is the only rate-controlling step, and there was no involvement of boundary layer or film diffusion in the adsorption process, if the intercept is zero and the linear plot passes through the origin. In Figure 10C, it can be confirmed that the intraparticle diffusion model did not totally control the adsorption process since there was no zero value obtained in the plot.

To investigate whether the adsorption process of Pb2+ ions onto the CFA/GO/WO3 nanocomposite is physisorption or chemisorption, the Arrhenius equation (eq 18) was applied by using a pseudo-second-order rate constant k2 [g/(mg·min)] at various temperatures.

\[
\ln k_2 = \ln A - \frac{E_a}{RT}
\]  
(14)

where A [g/(mg·min)] refers to the frequency factor, E_a (kJ/mol) is the activation energy of adsorption, R is the gas constant (0.008314 kJ/mol·K), and T is the temperature in Kelvin. E_a was obtained from the plot of ln k2 versus 1/T as presented in Figure 10D and estimated as 161.98 kJ/mol. This suggests chemisorption since E_a is higher than 40 kJ/mol.48

2.3.7. Adsorption Mechanism. The high removal efficiency was due to the increased surface area of the CFA/GO/WO3 nanocomposite and its robust functional groups that provided active sites for adsorption of Pb2+. The zeta potential result showed that the CFA/GO/WO3 nanocomposite had a negatively charged surface. This caused an electrostatic interaction that occurred between the negatively charged surface of the CFA/GO/WO3 nanocomposite and the positive charge of Pb2+.51 The FTIR spectrum (Figure 1Cb) shows that a successful adsorption of Pb2+ ions onto the CFA/GO/WO3 nanocomposite. XPS analysis was performed both pre- and post adsorption to further understand the mechanism of Pb2+ ion adsorption onto the CFA/GO/WO3 nanocomposite (Figures 5 & 6). Figure 5a shows that the characteristic peaks before adsorption are W 4f, Si 2p, W 4d, C 1s, O 1s, C KLL, O KLL, and W LMM, while new peaks appear at Pb 47/2, Pb 4d5/2, and 4d3/2, which confirm the successful adsorption of Pb2+ ions onto the CFA/GO/WO3 nanocomposite. The deconvolution of W 4d after adsorption presented a new peak at 268.56 eV associated with W4d3/2 as shown in Figure 6e. The XPS spectrum of O 1s shifted to 529.13 eV, and this was assigned to Pb–O after adsorption. This suggested that there was an interaction between Pb2+ ions and oxygen atoms present in W–O, hydroxyl group, and carbonyl group on the surface of the CFA/GO/WO3 nanocomposite during adsorption as shown in Figure 6c.39

Adsorbents derived from carbon-based materials have excellent adsorption properties because of the availability of functionalized oxygen groups that provide the adsorbent and adsorb with hydrophilicity and active sites. The functional groups present on the CFA/GO/WO3 nanocomposite can share electrons and bind with Pb2+ ions that form complexes.52 From the zeta potential, effect of pH, FTIR, and XPS results, it is evident that the adsorption of Pb2+ ions onto the CFA/GO/WO3 nanocomposite could involve the following reactions:

\[
\text{OH} + \text{Pb}^{2+} \rightarrow \text{OPb}^+ + \text{H}^+ 
\]  
(15)

\[
\text{W} - \text{O} + \text{Pb}^{2+} \rightarrow \text{Pb} - \text{O} + \text{W}^+ 
\]  
(16)
COOH + Pb^{2+} \rightarrow COOPb + H^{+} \quad (17)

From the above reactions, it is suggested that the mechanism of Pb^{2+} ion adsorption onto the CFA/GO/WO_{3}NRs nanocomposite is controlled by electrostatic interactions and complexation. The mechanism of Pb^{2+} ion adsorption onto the CFA/GO/WO_{3}NRs nanocomposite is shown in Scheme 1.

2.3.8. Effect of Coexisting Ions. Cu^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+} may coexist with Pb^{2+} ions in wastewater, and these could interfere with the adsorption of Pb^{2+} ions in aqueous media. Figure 11 presents the results of the effect of competing ions on Pb^{2+} ion removal using 0.04 g of CFA/GO/WO_{3}NRs nanocomposite while keeping the concentration of Pb^{2+} constant at 50 mg/L and varying the concentrations (10, 20, 30, 40, and 50 mg/L) of Cu^{2+}, Ni^{2+}, Cd^{2+}, and Mn^{2+}. The results revealed that the removal capacity of Pb^{2+} ions was the highest, and the CFA/GO/WO_{3} nanocomposite showed strong affinity to Pb^{2+} ions in aqueous media containing different competing ions. This may be attributed to factors such as difference in the hydration radius (Pb^{2+} = 4.01 Å, Ni^{2+} = 4.04 Å, Cu^{2+} = 4.19 Å, Cd^{2+} = 4.26 Å, and Mn^{2+} = 4.38 Å) and hydration energy (Pb^{2+} = −1481 kJ/mol, Mn^{2+} = −1760 kJ/mol, Cd^{2+} = −1807 kJ/mol, Cu^{2+} = −2010 kJ/mol, and Ni^{2+} = −2106 kJ/mol). According to the hydration radius and hydration energy data, the CFA/GO/WO_{3} nanocomposite would prefer Pb^{2+} ions over Ni^{2+}, Cu^{2+}, Cd^{2+}, and Mn^{2+} ions since ions with a smaller hydration radius and higher hydration energy are adsorbed faster and in higher quantities in multicomponent aqueous media.

2.3.9. Application of CFA/GO/WO_{3}NRs Nanocomposite in a Real Wastewater Sample. The synthesized CFA/GO/WO_{3}NRs nanocomposite was used for the removal of Pb^{2+} ions in a real wastewater sample collected in Reitvalle, Gauteng province of South Africa. The real wastewater source comprises sewage and mine water. The lead concentration was spiked to 50 mg/L before conducting the adsorption experiment. The results presented in Table 5 shows that the CFA/GO/WO_{3} nanocomposite is efficient in the adsorption of Pb^{2+} ions in a real wastewater sample.

Table 5. CFA/GO/WO_{3} Nanocomposite Application for Adsorption of Pb^{2+} Ions

| sample                  | concentration before spiking (mg/L) | removal after spiking (%) | pH |
|-------------------------|-------------------------------------|---------------------------|----|
| real wastewater         | 0.043                               | 100                       | 7.5|

2.4. Reusability Of Spent Adsorbent of the CFA/GO/WO_{3}NRs + Pb^{2+} Nanocomposite for Photocatalytic Degradation of Acetaminophen. The newly synthesized nanocomposite, CFA/GO/WO_{3}NRs nanocomposite, is very efficient for the removal of Pb^{2+} ions. The spent adsorbent (CFA/GO/WO_{3}NRs + Pb^{2+} nanocomposite) was obtained after adsorption of Pb^{2+} ion, and it was further investigated for its photocatalytic ability in the degradation of acetaminophen. The investigation was achieved using 5 ppm of acetaminophen in 500 mL of distilled water and 100 mg of catalyst at various time intervals of 0 to 180 min at pH 7 when exposed to visible light as shown in Figure 12A. The CFA/GO/WO_{3}NRs nanocomposite and blank experiments were also carried out to investigate the
photodegradation ability of the prepared nanocomposite before adsorption and the effect of photolysis on acetaminophen without a catalyst in the time interval of 0−180 min as shown in Figure 12B,C. The photocatalytic degradation of acetaminophen using the CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite at 180 min under visible light irradiation showed a degradation efficiency of 93% as shown in Figure 12Dc. The degradation efficiency of 86% was obtained after 180 min of irradiation for the CFA/GO/WO$_3$NRs nanocomposite as shown in Figure 12Db.

The result of photolysis revealed a degradation efficiency of 67% after 180 min of irradiation. This is because of the effect of light source as indicated in Figure 12Da. It has been reported in different studies that the light source could have an effect on the degradation of most pharmaceuticals including acetaminophen by photolysis without a catalyst. However, a lot of organic carbons could still be retained despite the effect of photolysis under visible light irradiation. The results showed that the CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite has a significant effect on the degradation of acetaminophen. The comparison of acetaminophen degradation by the CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite with other catalysts is shown in Table 6.

The rate of photocatalytic degradation of acetaminophen with photolysis, CFA/GO/WO$_3$NRs nanocomposite, and CFA/GO/WO$_3$NRs + Pb$^{2+}$ nanocomposite was calculated by using the pseudo-first-order equation as given below

$$\ln \left( \frac{C_f}{C_i} \right) = -Kt$$

where $C_i$ and $C_f$ are the initial and final concentrations of acetaminophen under visible light. The rate constants were calculated from the slope of the graph $\ln(C_f/C_i)$ versus times for photolysis without the catalyst ($= -0.00624$ min$^{-1}$), CFA/GO/
WO₃NRs nanocomposite (−0.0116 min⁻¹), and CFA/GO/WO₃NRs + Pb²⁺ nanocomposite with light (−0.01499 min⁻¹). The plots are shown in Figure 12Ea–c.

2.4.1. Photocatalytic Degradation Mechanism of Acetaminophen with the CFA/GO/WO₃NRs + Pb²⁺ Nanocomposite. The acetaminophen was first adsorbed on the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite under dark conditions for 30 min. Then, visible light was irradiated to start the photocatalytic reaction between the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite and acetaminophen at different times. The catalyst (conduction band and valence band) created very active O²⁻, ·OH, and ·O₂⁻ radicals after adsorption of visible light, and they were favored for degradation and mineralization of acetaminophen. The photocatalytic mechanism is shown in Scheme 2.

2.4.2. Investigation of Byproducts. The investigation of byproducts obtained after photodegradation is necessary as some final products may be more toxic than others. High-performance liquid chromatography–mass spectrometry (HPLC-MS) was used in the BG Mode to investigate the byproducts of acetaminophen photodegradation by the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite after degradation times of 30, 120, and 180 min as shown in Figure 13A–C. Figure 13A shows two peaks of interest in the positive scan spectrum after 30 min of degradation, which are the base peaks of acetaminophen (m/z 149) and fragmentation peak (m/z 117). A new peak was observed at m/z 107 (p-quinoimine) after a degradation time of 120 min, which is less toxic as shown in Figure 13B. Finally, after 180 min, majority of the peaks disappeared and others greatly reduced as indicated in Figure 13C. This confirms the photodegradation and complete mineralization of acetaminophen by the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite. The reaction pathway for the cleavage of acetaminophen is shown in Scheme 3.

Table 6. Comparison of Percentage Degradation of Acetaminophen by the CFA/GO/WO₃NRs + Pb²⁺ Nanocomposite with other Catalysts

| no  | catalyst                        | degradation (%) | references |
|-----|---------------------------------|-----------------|------------|
| 1   | ZnO commercial                  | 60              | 6          |
| 2   | ZnO nanopowder                  | 41              | 6          |
| 3   | N−ZnO                          | 80              | 7          |
| 4   | C−N codoped TiO₂ catalyst      | 70.39           | 53         |
| 5   | CFA/GO/WO₃NRs nanocomposite    | 86              | this study |
| 6   | CFA/GO/WO₃NRs + Pb²⁺ nanocomposite | 93         | this study |

Scheme 2. Mechanism of Acetaminophen Degradation with the CFA/GO/WO₃NRs + Pb²⁺ Nanocomposite under Visible Light Irradiation
3. CONCLUSIONS

A novel CFA/GO/WO₃NRs nanocomposite has been prepared through a hydrothermal technique and displayed excellent adsorption capacity for the effective removal of Pb²⁺ ions from aqueous solution and thereafter showed a new opportunity for the reusability of Pb²⁺ ion-loaded spent adsorbent as a photocatalyst. The prepared CFA/GO/WO₃NRs nanocomposite displayed a sorption capacity of 41.51 mg/g.

Figure 13. HPLC-MS of byproducts of acetaminophen photodegradation using the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite. (A) 30, (B) 120, and (C) 180 min.

Scheme 3. Proposed Fragmentation Pathway of Byproducts from Degradation of Acetaminophen Using the CFA/GO/WO₃NRs + Pb²⁺ Nanocomposite under Visible Light Irradiation

3. CONCLUSIONS

A novel CFA/GO/WO₃NRs nanocomposite has been prepared through a hydrothermal technique and displayed excellent adsorption capacity for the effective removal of Pb²⁺ ions from aqueous solution and thereafter showed a new opportunity for the reusability of Pb²⁺ ion-loaded spent adsorbent as a photocatalyst. The prepared CFA/GO/WO₃NRs nanocomposite displayed a sorption capacity of 41.51 mg/g. The adsorption
of Pb\(^{2+}\) ions onto the CFA/GO/WO\(_3\)NRs nanocomposite followed pseudo-second-order kinetics, and the Langmuir isotherm model had the best fit among the various isotherm models applied in this study. Furthermore, Pb\(^{2+}\) ion-loaded spent adsorbent (CFA/GO/WO\(_3\)NRs + Pb\(^{2+}\) nanocomposite) was reused efficiently as a photocatalyst for the degradation of acetaminophen with a degradation efficiency of 93%. In summary, due to the excellent adsorption of Pb\(^{2+}\) ions and efficient photodegradation ability of Pb\(^{2+}\) ion-loaded spent adsorbent, the CFA/GO/WO\(_3\)NRs nanocomposite is evidently viewed as a favorable material in environmental remediation. This now demonstrates a new opportunity where adsorbents used in the removal of heavy metal ions from aqueous media can be reused as photocatalysts in the degradation of organic pollutants, thereby avoiding secondary waste pollution due to the generation of spent adsorbents.

4. MATERIALS AND METHODS

4.1. Materials. Graphite powder, sodium tungstate dehydrate, lead nitrate, acetaminophen, hydrochloric acid, copper nitrate, cadmium nitrate tetrahydrate, sodium hydroxide, sulfuric acid, and phosphoric acid were supplied commercially by Sigma-Aldrich. The CFA was obtained from a thermal power station in South Africa. Unless otherwise stated, all chemicals used in this study were of analytical grade.

4.2. Synthesis of CFA/GO/WO\(_3\)NRs Nanocomposite. First, 100 g of raw CFA was mixed with 4M HCL in 120 mL of deionized water. It was stirred for 4 h, centrifuged, and oven dried overnight at 90 °C for the removal of soluble compounds and activation of the CFA. GO nanosheets were prepared by modification of a method reported elsewhere,\(^\text{19}\) with changes to graphite (5 g), KMnO\(_4\) (18 g), H\(_2\)SO\(_4\) (360 mL), and phosphoric acid (40 mL) under reflux at 60 °C for 12 h. Then, the reaction was quenched with 30% H\(_2\)O\(_2\) and centrifuged with water, ethanol, and diethyl ether to remove unreacted impurities, and the black brown precipitate was sonicated for 30 min and oven dried at 50 °C overnight.

Thereafter, 5 g of NaWO\(_4\)\(\cdot\)2H\(_2\)O, 4 g of GO, and 3 g of CFA were mixed in 50 mL of deionized water and stirred for 30 min. The mixture was transferred into a 100 mL Teflon-lined autoclave at 150 °C 12 h. The CFA/GO/WO\(_3\) nanocomposite was obtained by centrifuging the suspension and oven drying at 90 °C overnight as displayed in Scheme 4.

4.3. Characterization of CFA/GO/WO\(_3\) Nanocomposite. Different techniques were applied to investigate the properties of the CFA/GO/WO\(_3\) nanocomposite before and after adsorption. The morphology of the nanocomposite was
examined using scanning electron microscopy (SEM, Tescan-vega 3× mu). Confirmation of the prepared CFA/GO/WO₃NRs nanocomposite and particle size were obtained using TEM (JEOL JEM-2100F) at 90 kV. DRS-UV was used to determine the band gap energy of the CFA/GO/WO₃ nanocomposite before and after adsorption [Schimidzu UV-1208 model (Japan)]. FTIR was used to investigate the functional groups [PerkinElmer PE1600 FTIR spectrophotometer (USA)] within the range of 4000–400 cm⁻¹, and the pellet was prepared with KBr. The measurement of zeta potential was carried out using a Malvern ZetasizerNanoZS 90. The crystal structures of raw CFA and CFA/GO/WO₃ nanocomposite were obtained using XRD. XPS analysis was conducted using a Kratos Axis Ultra device (Kratos, UK), monochromatic Al Kα radiation. The BET technique was applied to investigate the surface area and pore size distribution under nitrogen adsorption–desorption using a Micro-metrics, ASAP 2020 analyzer.

4.4. Adsorption Experiments. The effectiveness of the CFA/GO/WO₃ nanocomposite for Pb²⁺ ion removal was studied in a series of batch adsorption experiments. A Pb²⁺ stock solution (1000 mg/L) was prepared by dissolving an exact amount of Pb(NO₃)₂ in 1000 mL of deionized water and diluting to the desired concentrations. In a typical batch adsorption study, 30 mL of the metal solution was placed in a 100 mL plastic bottle containing the adsorbent and was agitated on a thermostatic incubator shaker (Separation Scientific, South Africa) at 200 rpm shaking speed for 1 h. The initial pH of Pb²⁺ ion solutions was achieved by adding 0.1 M NaOH and HCl solutions before the addition of the CFA/GO/WO₃ nanocomposite. The effects of the CFA/GO/WO₃ nanocomposite dosage, pH, and concentration of Pb²⁺ ions, contact time, and temperature were investigated to optimize the adsorption conditions. Different dosages of the CFA/GO/WO₃ nanocomposite ranging from 0.02 to 0.3 g were suspended into 30 mL of Pb²⁺ ions at room temperature. The solid was immediately filtered through 0.45 μm membrane filters when the reaction ended, and the residual Pb²⁺ ions concentration was measured using inductively coupled plasma–atomic emission spectroscopy (ICPE-9820 plasma atomic emission spectrometer, Shimadzu). The adsorption efficiency and capacity of the synthesized adsorbent were determined by the equations below.

\[
q_t = \frac{(C_0 - C_t)V}{W} \quad (20)
\]

\[
q_e (\text{mg/g}) = \frac{(C_0 - C_e)V}{W} \quad (21)
\]

where \(C_0\) (mg/L), \(C_t\) (mg/L), and \(C_e\) (mg/L) represent the initial concentration, the equilibrium concentration, and the concentration at time \(t\) of Pb²⁺ ions, \(q_t\) (mg/g) and \(q_e\) (mg/g) are the quantity of Pb²⁺ ions adsorbed by the CFA/GO/WO₃NRs nanocomposite at time \(t\), \(V\) (L) is the volume of Pb²⁺ ions, and \(W\) (g) is the total mass of the CFA/GO/WO₃ NRs nanocomposite used during adsorption. To determine the validity and reproducibility of results, all experiments were carried out in triplicate.

4.5. Investigation of Coexisting Ions. Pb²⁺ selectivity was studied by using an initial Pb²⁺ ion concentration of 50 mg/L while varying the concentrations (10, 20, 30, 40, and 50 mg/L) of Cu²⁺, Ni²⁺, Cd²⁺, and Mn²⁺ in the same solution and a volume of 30 mL. The optimum pH condition was used and the adsorbent dosage was 0.04 g.

4.6. Photocatalytic Investigation of the Spent Adsorbent for Degradation of Acetaminophen. The investigation of the photocatalytic ability of the lead-loaded spent adsorbent (CFA/GO/WO₃+Pb²⁺) and the CFA/GO/WO₃ NRs nanocomposite was achieved by adding 100 mg of CFA/GO/WO₃+Pb²⁺ into 5 mg/L acetaminophen solution in a glass reactor. A 250 HW lamp was used as the source of visible light. The mixture of the CFA/GO/WO₃ NRs + Pb²⁺ nanocomposite and the CFA/GO/WO₃NRs nanocomposite as well as acetaminophen was stirred magnetically for 30 min in the dark prior to photodegradation to enable the adsorption equilibrium of acetaminophen. Cooled water was circulated all through the experiments via the water inlet of the photo reactor to regulate the temperature. Samples of 5 mL were taken at 30 min time intervals using a 0.45 μm syringe filter for the separation of the CFA/GO/WO₃NRs + Pb²⁺ nanocomposite and the CFA/GO/WO₃NRs nanocomposite from the solution. A UV–visible spectrophotometer was used to obtain the concentration of acetaminophen using its absorption peak at 243 nm. In order to confirm reproducibility, all experiments and measurements were carried out in triplicate.

The removal efficiency of acetaminophen was evaluated as follows

\[
\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100
\]

where \(C_i\) is referred to the initial concentration of the solution and \(C_f\) is the concentration after photodegradation, all in mg/L.

The degradation of byproducts of acetaminophen was evaluated by HPLC-MS (SHIMADZU Nexera X2HPLC system). The mobile phase was used as 0.2% formic acid, water, and acetonitrile at 0.3 mL/min system). The mobile phase was used as 0.2% formic acid, water, and acetonitrile at 0.3 mL/min flow rate with reversed phase (150 mm × 2.0 mm, 5μm, PhenomenexLUNA C18).

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E.C.U. and E.P. have equally contributed. The project was supervised and guided by Prof. Kriveshini Pillay.

**Notes**

The authors declare no competing financial interest.
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