



Assessment of Removal Efficiency of Ag₂O-TiO₂-Kaolinite Clay Hybrid Nanocomposite developed for the treatment of Mn(II), Fe (III), Pb(II) And Cu(II) in Mining Wastewater

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ABSTRACT

This study considered the synthesis of Ag₂O-TiO₂-kaolinite-clay nanocomposite by the combination of green and wet impregnation method, which involves the reduction of silver nitrate and titanium tetra isopropoxide to nanoparticles with aqueous extract of *Parkia biglobossa* leaf. These were then immobilised on acid-activated kaolinite clay. The prepared nanomaterials' phase structure, morphology, chemical composition, and oxidation states were determined using X-ray diffraction (XRD), high resolution scanning electrode microscopy (HRSEM), and X-ray photoelectric spectroscopy (XPS). The ability of the nanocomposite prepared to adsorb four heavy metal ions (Mn (II), Fe (III), Pb (II), and Cu (II)) from mining wastewater was examined by varying the contact time. The XRD pattern of the Ag₂O-TiO₂-clay reveals the synthesis of the rutile phase of TiO₂ embedded in the kaolinite clay, while the HRSEM shows evenly distributed arrangement of hemispherical stacks of kaolinites. The states of oxidation of Ag and Ti revealed by the XPS are +1 and +4 respectively either as binary or ternary nanocomposite. The Ag₂O-TiO₂-clay nanocomposite adsorbed 99.85%, 97.85% 95.18%, and 40% of Fe(III), Mn (II), Cu(II) and Pb(II) ions at 120 min from the mining wastewater respectively. The synergetic efforts of the Ag₂O, TiO₂, and acid-activated kaolinite clay was found responsible for the adsorptive capability and post-separation possibility of the Ag₂O-TiO₂-clay nanocomposite.

Keywords: Adsorption, Characterisation, Kaoline, Mining wastewater, Nanocomposite.

1.0 INTRODUCTION

There is a great concern about water safety and availability due to industrial activities that generate heavy metals and pollute water bodies (Wazwaz *et al.*, 2019). Amidst the heavy metals generating industries are; pharmaceutical, paints, electroplating, and mining industries. Heavy metals generated from mining activities include; Pb, Fe Zn, Cd, Mn, As, and Cu which are linked to dangerous environmental issues threatening life on earth (Hussain & Ali, 2021). These heavy metals are highly mobile, non-biodegradable, recalcitrant, and toxic at low concentrations and their continuous presence in the environment can cause physiological disturbances to both plants and animals (Balali-Mood *et al.*, 2021). Exposure to heavy metals such as Pb, Zn, Cd, Mn, and Cu in excess has been responsible for diarrhoea, abdominal pain, lethargy, nausea, anaemia, and eventual death (Ajala, Abdulkareem, Tijani, & Kovo, 2022), therefore, these heavy metals must be removed.

Many wastewater treatment techniques have been employed for heavy metal removal in wastewater. These include; electro dialysis, catalytic processes, chemical precipitation, membrane processes, ion exchange processes, and adsorption process. (Hussain & Ali, 2021) The adsorption process is a preferred alternative because of its high efficiency and simplicity (Adebayo, Adegoke, & Sidiq, 2020). Adsorption with nanoparticles and nanocomposites of chitosan, carbon nanotubes, zinc oxide, iron oxide, titanium oxide, and silver oxides have gained pre-eminence because of their unique physiochemical properties (Kumari, Alam, & Siddiqi, 2019). These nanomaterials are also considered all-encompassing, due to their antimicrobial properties and non-production of harmful disinfection by-products like conventional chemical disinfectants (Sushman & Richa, 2015).

Among the nanomaterials, TiO₂ nanoparticles and their composites have been employed for the mineralization and degradation of organic compounds, dyes, and other contaminants in water remediation processes (Dontsova *et al.*, 2020). Despite its uniqueness, the low surface area and agglomeration of TiO₂ limits its industrial applications as a

nano-adsorbent (Akinawo, 2019). To overcome the limitations, it is therefore doped with other materials like clay, silver, silver oxide nanoparticles (AgNPs/Ag₂ONPs) (Akinawo, 2019; Ajala *et al.*, 2022). Ag₂ONPs have wide applications as antimicrobial agents and demonstrated excellent catalytic performance in the degradation of anthropogenic pollutants present in the environment (Arya *et al.*, 2018; Christopher, Saswati, & Ezilrani, 2015). Meanwhile, AgNPs and Ag₂ONPs have been previously successfully used to treat wastewater by incorporating them into materials such as; polyurethane foams, carbon/polymeric nanofibres, and clays (Kyomuhimbo *et al.*, 2019). Hence, the combination of silver with other metal nanoparticles such as TiO₂ can enhance the adsorption capacity for wastewater treatment (Yadav *et al.*, 2017). In addition, a possible combination of clay with metal nanoparticles is expected to perform multi-functionality such as adsorption, catalysis, disinfection, and overcome post-separation problems during the treatment of wastewater (Shivaraju, Egumbo, Madhusudan, Anil Kumar, & Midhun, 2018).

Clays possess desired properties of a good starting material for wastewater treatment and nano filter production. These properties include high cation exchange capacity and ease of surface modification to obtain the desired functionality required of a good adsorbent (Awasthi, Jadhao, & Kumari, 2019). Clays of different origins, compositions, and modifications have been used as adsorbents and as support for nanoparticles to treat wastewater (Hajjaji *et al.*, 2018). However, the use of silver immobilised titanium oxide nanocomposite supported on clay has not been reported for heavy metal removal in mining wastewater treatment. Therefore, this study focuses on the treatment of mining wastewater using silver-doped titanium oxide nanocomposite supported on clay to act as an adsorbent for the removal of heavy metal ions.

2.0 MATERIALS AND METHODS

2.1 Material collection

Analytical silver trioxo nitrate (V) (>97%), titanium (IV) isopropoxide solution (>98%), sodium hydroxide, hydrochloric acid (37%), and tetraoxosulphate (IV) acid (98%) were obtained from Sigma Aldrich. The fresh leaves of *Parkia biglobossa* were obtained from different locations in Ilorin, Kwara State (Nigeria) Metropolis and certified by a plant taxonomist. Clay samples were collected from deposits in Akerebiata, Ilorin. The mining wastewater was collected from artisanal gold mine in Chanchaga Local government Area, Minna, Niger State, Nigeria. The mining wastewater was collected into a clean 5000 cm³ polythene bottle, transferred to the laboratory, and stored in a refrigerator before investigation. The heavy metal concentrations were quantified by Atomic Absorption Spectroscopy machine (AAS) (PG990).

2.2 Synthesis of Silver oxide/Titanium (IV) oxide immobilized on acid-activated kaolinite clay

The nanoparticles of TiO₂ were synthesized using the method of Ajala *et al.* (2022) with 50 cm³ of *Parkia biglobossa* aqueous leaves extract, which has been confirmed rich in phenolic and flavonoid content, 50 cm³ of titanium (IV) isopropoxide solution pH 8, stirred for 2 h on a magnetic stirrer at a speed of 2000 rpm. There was a development of precipitates accompanied by the color change. The resulting TiO₂ nanoparticles cake was filtered, washed, aged, oven-dried, and later calcined in a muffle furnace for 2 h at 550°C. Thereafter, 12 cm³ of 0.005 M AgNO₃ aqueous solution was measured into a 250 cm³ beaker followed by the addition of 6 cm³ of aqueous leaf extract. The solution pH was adjusted to 8 using 2 M NaOH solution and 6 g of the already synthesized TiO₂ nanoparticles was added to the mixture. The mixture was stirred at 1000 rpm speed for 2 h, the solution completely changed from pale white to dark grey which indicated the reduction of metallic silver and the complete reduction of Ag⁺ to Ag⁰. Evidence of silver loading onto titanium dioxide nanoparticles was also confirmed by the change in colour from white TiO₂ nanoparticles to grey Ag₂O-TiO₂ slurry. The mixture was left overnight to age, oven dried at 100°C for 1 h before calcination for 2 hours at 450°C in the furnace to obtain Ag₂O-TiO₂ nanocomposites. The Ag₂O-TiO₂ nanocomposites were immobilized on 40 g of activated clay already prepared using the method of Ajala *et al.* (2022) via wet impregnation technique. The resultant slurry was calcined at 450°C to produce Ag₂O-TiO₂-clay hybrid nanocomposite.

2.3 Characterization of Ag₂O-TiO₂ and Ag₂O-TiO₂-clay hybrid nanocomposite

A Bruker AXS D8 Advance X-ray diffractometer (XRD) employing Cu K radiation was used to examine the phases and crystallite sizes of the produced nanomaterials. The morphological disposition and elemental composition of the samples were also examined using a Zeiss Auriga HRSEM equipped with energy dispersive spectroscopy (EDS). The oxidation states of the surface elements of Ag₂O-TiO₂ nanoparticles and Ag₂O-TiO₂-activated clay nanocomposites were investigated using X-ray photoelectron spectroscopy (XPS) with monochromated Mg K (1,253.6 eV) operated at 300 W and 15 eV.

2.4 Batch adsorption of metal ion onto Ag₂O-TiO₂-activated clay nanocomposites.

Batch adsorption treatment of the mining wastewater was carried out using the synthesized Ag₂O-TiO₂-activated clay. The process was carried out at temperature 30°C and 0.5 g adsorbent dose, while contact time was varied between 20 - 180 min to study the effect of contact time on the adsorption process. In doing this, 100 cm³ of the mining wastewater was measured into 0.5 g of the Ag₂O-TiO₂-activated clay nanocomposite in a 250 cm³ flask, the experiments were performed in duplicates. Sampling was done at an interval of 20 min and the resulting mixture was filtered. The

supernatant was analyzed for unwanted metal ions (Fe(III), Pb(II), Zn(II), and Cu(II) concentration by the AAS. Equations 1 and 2 were used to calculate the adsorbed phase concentration (q_t , in mgg^{-1}) at a time (t) and the percentage of metal ion removal, given as:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (2)$$

Where C_o and C_t represents the initial, final, and equilibrium metal ion concentrations in milligrams per liter (mgL^{-1}) respectively; V represents the volume of the water sample (L) and m is the mass (g) of adsorbent used. (Guillaume, Chelaru, Visa, & Lassiné, 2018).

3.0 RESULTS AND DISCUSSION

3.1 Metal ion concentration in wastewater

The heavy metal analysis from the artisanal gold mining wastewater revealed that, the water has heavy metal concentrations of 20.02 mg/L Fe (III), 4.29 mg/L Mn (II), 0.31 mg/L Cu (II), and 0.98 mg/L Pb (II) ions. These results are higher than the permissible limit (heavy metal) for industrial and drinking water by the WHO and NIS respectively (WHO, 2017) thus, the need for the mining wastewater treatment with Ag₂O-TiO₂-clay hybrid nanocomposite.

3.2 Characterisation results of synthesised adsorbents

3.2.1 XRD analysis

Figure 1a and b are the XRD spectral of the nanocomposites, which confirmed the effective interaction between the kaolinite clay structure and the rutile-phased titanium (IV) oxide doped with silver oxide nanoparticles. In Figure 1a, there is the presence of peaks at angle 2θ and corresponding crystal planes of 27.4° (110), 36.1° (101), 39.2° (200), 41.2° (111), 44.0° (210), 54.3° (211), 56.8° (220) and 69.8° (112), these are assigned tetragonal, rutile-phase titania, with JCPDS number 00-021-1276 (Key: K=kaolin, R=rutile-TiO₂, Q=quartz C=calcite).

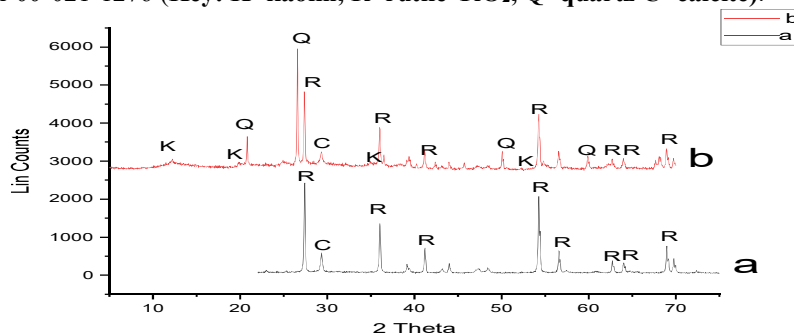


Figure 1: XRD spectral of (a) Ag₂O-TiO₂ (b) Ag₂O-TiO₂/clay nanocomposite

The Ag₂O peaks were not shown on the XRD pattern, which may be attributed to the low concentration and occurrence of silver oxide in the reduced form as nanoparticles (Shameli, Ahmad, Yunus, & Ibrahim, 2011). The non-detection of Ag₂O by the XRD is perhaps due to insufficient Ag₂O content in the composite to form an observable crystalline structure which follows research findings (Bagheri, Ramimoghdam, Yousefi, & Hamid, 2015). In Figure 1b are diffraction peaks at 2θ values of 12.36° , 19.92° , 24.80° and 38.40° with miller indices; (001), (020), (002) and (-113) respectively corresponding with JCPDS 01-079-1570, which shows the clay is kaolinite. At 2θ values of 20.93° (100), 26.59° (101), and 40.22° (111), there are strong and relatively powerful diffraction peaks in agreement with the literature (JCPDS card no 00-083-0539) indicative of quartz presence in the clay. The indices of; 27.52° (110), 36.08° (101), 41.22° (111), 44.05° (210), 54.32° (211), 56.70° (220), 62.90° (002), 64.03° (310), 69.28° (301) and 70.14° (112) matched well with a typical rutile phase of TiO₂ nanoparticles having JCPDS number, 00-021-1276. The XRD patterns of Figures 1a and b, obviously show that immobilizing the Ag₂O-TiO₂ nanoparticles on Ag-TiO₂-clay nanocomposites did not cause phase transformation from rutile to either anatase or brookite, but the TiO₂ rutile phase maintained. Only the various intensities of rutile-TiO₂ peaks were reduced and shifted, in Figure 1b. The diffraction peaks earlier noticed on Ag-TiO₂ were similarly represented on the Ag-TiO₂-clay nanocomposites with the addition of kaolinite peaks. These peaks are evidence of clear interaction between the Ag₂O-TiO₂-clay composite.

3.2.2 SEM/EDS results

The HRSEM image of the Ag₂O-TiO₂ and Ag₂O-TiO₂-clay is presented in Figure 2a (i) and (ii). The image shown in Plate 2a (i) reveals the uniformly distributed spherical morphology. The structure of the Ag₂O-TiO₂ maintains a cage-bell structure reported for TiO₂ without destruction after modification with Ag₂O nanoparticles (Guo *et al.*, 2013).

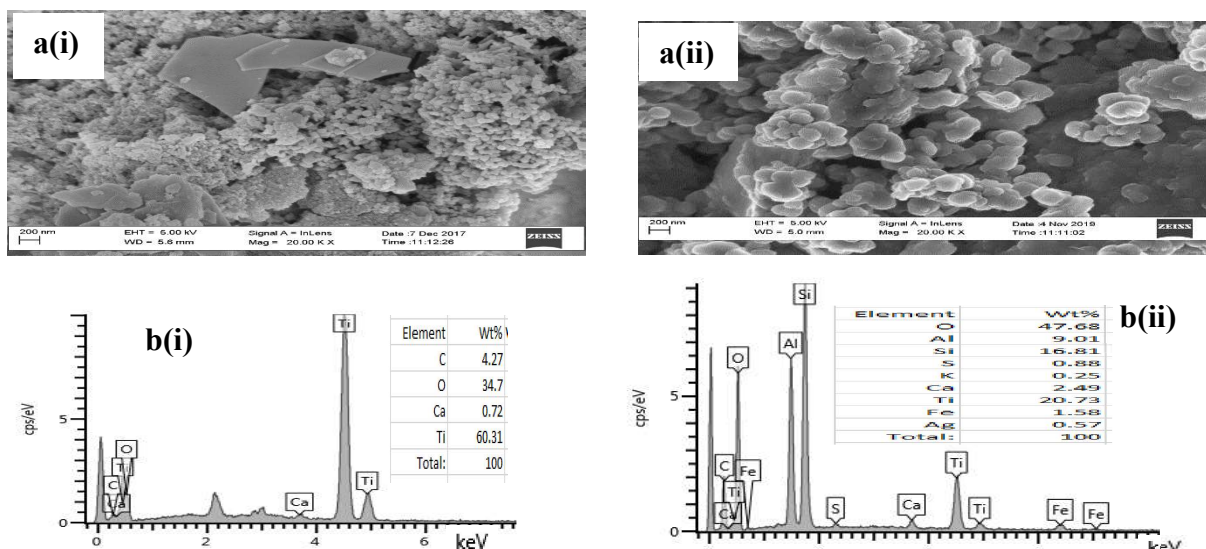


Figure 2: (a) SEM images of (i) Ag₂O-TiO₂ (ii) Ag₂O-TiO₂/clay (b) EDS images of (i) Ag₂O-TiO₂ (ii) Ag₂O-TiO₂/clay

The image reveals porosity and also showed that the silver deposition did not cause lattice distortion on the synthesized Ag₂O-TiO₂ (Pham & Lee, 2014). This indicates good silver dispersion on the TiO₂ surface, as well as the fact that the doping impact affects the morphological layout of the nanoparticles generated (Oguzhan, Yildiz, Semih, & Ozge, 2016). The morphology of the theAg₂O-TiO₂-clay in Figure 2a (ii) shows an evenly distributed and interstitial arrangement of the clay lattice, which consists of hemispherical stacks of platelets structures of porous kaolinites similar to previous work (Mustapha *et al.*, 2019). The elemental composition of the Ag₂O-TiO₂ (ii) Ag₂O-TiO₂-clay in Figure 2b (i) and (ii) at binding energy between 0-20 keV revealed the presence of C, O, Al, Si, S, K, Ti, Fe, Ag and Ca. Figure 2b (i) shows the presence of high composition of Ti (60.31%) with Oxygen (34.70%) in the nanocomposite. There is a complete absence of Ag, probably due to its minimal concentration in the doped composite, similar to the report of (Petrik, Missengue, Fatoba, Tuffin, & Sachs, 2012) and which corroborates the XRD results. In the Ag₂O-TiO₂-clay spectral, the presence of Ag was confirmed, having 0.57%, which shows that Ag was doped on the structure. The high percentage of Ti (20.73%) is attributed to the doping of TiO₂ and its even distribution in the composite matrix. This is similar to the previous report where Zn was immobilised on the kaolinite clay surface (Mustapha *et al.*, 2020). The high percentage of oxygen reveals that the Si, Al, Fe, C, Ti, and Ag are present in a combined state as oxides. The entire element in Figure 2bii shows that the sample is an alumino-silicate material having Ag₂O, and TiO₂ incorporated into the activated clay.

3.2.3 XPS analysis

The condition of oxidation number on the surface and orbital of the elements included in the samples were determined by XPS analysis of Ag₂O-TiO₂ nanoparticles and Ag₂O-TiO₂-clay nanocomposite (Figure 3). Figures 3a (i) and (ii) are the general survey spectrum, while 3b and 3c are the peak deconvoluted for Ti and Ag in the (i) Ag₂O-TiO₂ and (ii) Ag₂O-TiO₂-clay respectively. The XPS of the Ag₂O-TiO₂ sample (Fig.3 ai), reveals the presence of titanium, oxygen, silver, and carbon at different binding energies on both spectra.

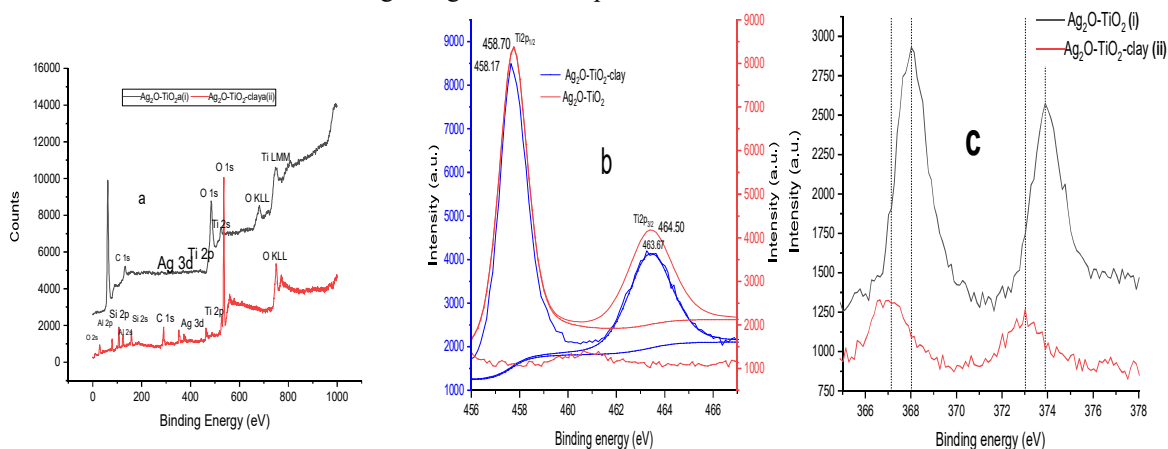


Figure 3: (a) General XPS spectrum (b) deconvoluted spectral of Ti (c) Ag (i) Ag₂O-TiO₂ and (ii) Ag₂O-TiO₂-clay

The presence of Ag 3d at binding energies 368.80 eV and 369.20 reveals evidence of Ag₂O doping on TiO₂ nanoparticles at 464. 50 eV and 463.67 eV in Figures 3a (i) and (ii) respectively. The titanium LMM Auger transition exhibits an

intense peak in the region of 880 eV and 760 eV indicating the presence of the TiO₂ crystal. Figure 3 a(ii) reveals the presence of Ag₂O doped on the alumina-silicate clay structure which could not be seen in the XRD spectra. Figures 3 b(i), (ii) and 3 c(i), (ii) are the deconvoluted XPS spectra of Ti and Ag in Ag₂O-TiO₂ and Ag₂O-TiO₂-clay samples, respectively. The figures reveal the presence of doublet peaks of Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons in each of the two samples. These were located at similar binding energies of 458.70 eV and 464.50 eV on b(i) while at 458.17 eV and 463.67 eV on b(ii). The peaks show the difference of ~ 6 eV (5.8 and 5.58 eV) on Ag₂O-TiO₂ and Ag₂O-TiO₂-clay respectively, which is an indication of the existence of Ti as TiO₂ framework in the oxidation state of +4, irrespective of the composite. Figure 3ci reveals the presence of two intense peaks at energy levels of 368.5 eV and 373.9 eV. The split peak observed were assigned to Ag 3d_{5/2}(368.5 eV) and Ag 3d_{3/2}(373.9 eV). The binding energy difference between the split 3d doublet and the singlet is roughly 6.0 eV. This indicates that the oxidation state present on the surface of Ag is zero and not the metallic silver as present in AgNO₃. Irrespective of the ionic radius disparity between Ag (0.115 nm) and Ti (0.061 nm), it is clear that some Ag⁰ species may have penetrated the TiO₂ framework, implying a mutual interaction between the dopant and the doped.

3.3 Adsorption study

3.3.1 Effect of contact time

The result of the variation of contact time effect on the removal of Mn (II), Fe(III), Pb (II), and Cu (II) ions by Ag₂O-TiO₂-clay nano adsorbent is revealed in Figure 4. The percentage removal of Mn (II), Fe (III), and Cu (II) ions from mining wastewater increased drastically within the first 60 mins then became gradual from 80 to 120 minutes and thereafter the adsorption became constant for the four metal ions considered in this study. The rapid elevation in percentage removal of the metal ions at the onset of the adsorption exercise was ascribed to the high number of vacant adsorptive surfaces on Ag₂O-TiO₂-clay and this resulted in a higher solute concentration gradient (Mnasri-Ghnmimi & Frini-Srasra, 2019). As time progresses between 80 to 120 minutes, the adsorptive surfaces became saturated with metal ions and further adsorption became difficult (Kazak, Eker, Bingol, & Tor, 2018). The low removal of Pb(II) ions may be attributed to its large ionic radii (0.06nm> Mn (II) 0.072 nm> Cu (II) 0.073nm> Pb (II)0.119nm) because, ions with a large ionic radius diffuse slower (Ajala et al, 2022).

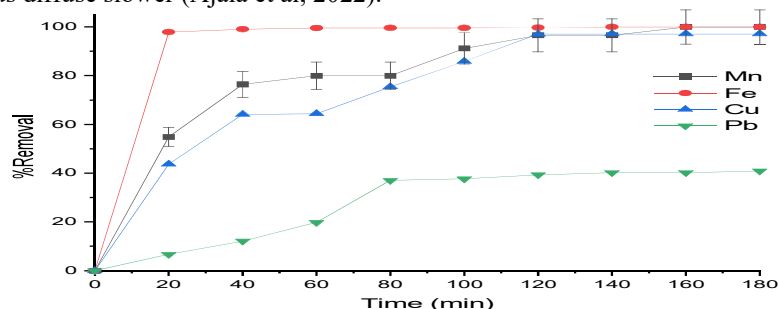


Figure 4: Effect of contact time on percentage removal of the metal ions.

4.0 CONCLUSION

The Ag₂O-TiO₂ and Ag₂O-TiO₂-clay nanocomposite materials were successfully synthesized by a simplistic, green, efficient, and environment friendly procedure. The findings from this study confirmed the presence of Ag₂O and TiO₂ in the interlayer of acid-activated kaolinite clay. The synthesised titanium was confirmed rutile TiO₂, in the +4 oxidation state in both Ag₂O-TiO₂ and Ag₂O-TiO₂-clay nanocomposites matrices and has a large surface area. The adsorptive effects studied revealed that time of contact affect the rate of removal of the metal ion onto the Ag₂O-TiO₂-clay surface. The Ag₂O-TiO₂-clay nanocomposite can therefore be used for the efficient removal of Mn (II), Fe (III), Pb (III) and Cu (II) ions from mining wastewater.

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