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Synthesis and characterization of Al-magadiite material: ions exchanged and effect of copper sources on antimicrobial activity

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Abstract. In this paper, the Al-magadiite synthesized by hydrothermal method. It is then used to prepare three copper exchanged materials using copper nitrate, copper chloride, and copper sulfate salts. The materials obtained were characterized and applied as antibacterial and antifungal against pathogen strains. The characterization methods showed the presence of four coordinated of aluminum atoms in the magadiite framework. The presence of aluminum leads to the total exchange of interlayer sodium cations. Otherwise, the copper exchange rate is influenced by the nature of the counter-ion used. Indeed, the exchanged rate increase in the sense of copper nitrate>copper chloride>copper sulfate. The chemical analysis shows that the ion exchange of Al-magadiite with copper salts is accompanied with dehydration of Cu-exchanged materials. This result was confirmed XRD diffraction, chemical analysis, and FTIR spectroscopy. This dehydration depends on the nature of the counter ion increase also in the sense of copper nitrate>copper chloride>copper sulfate. Tested as antibacterial and antifungal materials against pathogens strains all the copper exchanged materials exhibits a good antibacterial activity against Gram-positive bacteria which increased with increasing the copper content of a sample. The best activity was observed in the exchanged sample prepared from copper nitrate. However, a low or no activity is observed against Gram-negative bacteria.

Keywords: Al-magadiite, Copper II, counter-ions, ion-exchange, layer silicates, antimicrobial activity.

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1 Introduction

Metallic ions such as Ag^+, Cu^{2+}, Ni^{2+}, Ce^{3+} and Zn^{2+} were widely applied against different pathogen bacteria due to their intrinsic antibacterial activities [1-4]. Advanced by human health and environmental concern and economic consideration, these antibacterial metals were not used alone [5-7]. To overcome these environmental and public health problems, these metal ions were loaded into solid supports such as clays, lamellar silicates, zeolites, etc [8-12]. These charged solids must ensure the non-release of these metals in the medium while keeping or improving their antibacterial or antifungal activity. As shown in the literature, copper compounds such as $CuSO_4$ and $Cu(OH)_2$ were widely used as conventional inorganic antibacterial materials [13]. Nevertheless, due to copper resistance observed for some bacteria

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strains, it was found that a large amount of Cu^{2+} must be used to obtain a good antibacterial activity. Thus, the development of new materials capable of containing within them a controlled quantity of copper can solve the problems inherent to this resistance reference

The hydrous layered silicates family contains magadiite, kenyaite, makatite, kanemite, octosilicate, and silhydrite. The structure of these materials is constituted of a very reactive silicic acid layer and easily exchangeable interlayer hydrated sodium cations. The difference between these solids lies in the thickness of the silicate sheet and consequently in their basal spacing, d_{001}[14-16]. The successful syntheses of these minerals in the laboratory have given them more importance [14, 17-20]. Magadiite, the most studied among the layered polysilicate with the ideal formula ($Na_2Si_{14}O_{29}$ nH_2O) and an interlamellar distance of 15.65 Å which evolves with water content, thus revealing a swelling character [21]. the negative charge also the layer charge density is relatively high (~220 meq/100 g magadiite) gives more interesting and unique properties compared to smectites [15, 22, 23]. These properties are at the origin of new composites based magadiite materials which have been prepared by intercalation [18, 24-29], interlayer grafting, silylation and pillaring reactions [30-33]. These resulting composite materials are applied as adsorbents [27, 34-38], catalysts [39-41], molecular sieves[42] and exfoliation materials [43-45]. However, the presence of silanol groups on the surface of magadiite is considered to be very weak Brønsted acid sites [41, 46]. In order to increase the acidity of this material, researchers developed methods to insert trivalent element such as Al^{3+}, Ga^{3+}, and B^{3+} in the silicate layer (reference). This substitution of a part of silicon atoms constituted a good approach to generate new properties such as a variable surface acidity which can provide a wide range of applications [47, 48].

To our acquaintance, no work mentioning preparation and use of metal-exchanged Al-magadiite as antibacterial or antifungal agent has been reported so far while all the properties mentioned above place it in position for to be an ideal candidate for such domain. In this context, the present work reports the exchange reaction of Al-magadiite with different sources of copper cations by using $Cu(NO_3)_2$, $CuCl_2$ and $CuSO_4$ salts. The prepared materials were characterized by the X-ray diffraction (XRD), Chemical analysis (EDS), Scanning Electron Microscopy (SEM), thermogravimetric analysis (TG), Fourier Transform Infrared (FTIR) spectroscopy and UV-visible Diffuse Reflectance spectroscopy (UV-Vis DR), all the prepared solids are applied as antibacterial and antifungal materials against pathogen strains.

2 Experimental

2.1 Characterization

X-ray powder diffraction (XRD) patterns were recorded in the 2θ range of 02─70° at a scan rate 2º/min, on a Philips diffractometer model PW 1830, with Ni-filtered CuKα (λ= 1.5406 Å) radiation operated at a tube voltage of 40 kV and a tube current of 30 mA. The Fourier Transform Infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} on a JASCO 4100 spectrometer. To study the morphology and provided the copper content of the prepared samples the HIROX SH 400 M SEM-EDS BRUKER scanning electron microscope equipped with EDS was used. The sample was coated with carbon and attached to sample holder with carbon tape. UV-Visible diffuse reflectance (UV–Vis DR) spectroscopy spectra were recorded on a Specord 210 Analytik Jena spectrometer with a holmium oxide filter. Thermal analysis (TG-DTA) was performed in air using a Start Pyris DTA-TGA analyzer. All the samples were heated to 1000°C at heating rate of 10°C min^{-1}.

2.2 Preparation of Al-magadiite

Al-magadiite samples were synthesized by hydrothermal method from reaction mixtures of molar stoichiometric composition SiO_2: NaOH: Al_2O_3: H_2O of 100: 20: 3: 2000. The synthesis reaction is carried out as follows: The sodium hydroxide is dissolved first in deionized water and the aluminum source is added under magnetic stirring until complete dissolution. Then, the silica gel is added, with stirring at room temperature, to the previous solution. After aging at room temperature for 24 hours, the resulting hydrogel is transferred to a Teflon reactor and heated at a temperature of 150°C for 5 days. The solid sample, obtained, named Al-magadiite, was recovered by filtration, washed with deionized water to achieve neutral pH and then dried at 80°C for 12h.

2.3 Preparation of exchanged Al-magadiite (Cu) with differents source of copper cations

In order to study the effect of the counter ion on the intercalation of the as-synthesized Al-magadiite sample, three solutions of copper II were prepared from three different cooper salts, i.e. cooper nitrate, copper chloride and copper sulfate solutions. The intercalation was carried out by ion-exchange method as follows: 1 g of Al-magadiite was suspended in deionized water and stirred for 30 minutes. Then, the source of copper (II) ions solution was added. The reaction mixtures obtained were vigorously stirred at room temperature for 24 hours at a temperature of 30°C. The final pH was 5.3. The resulting solids, named respectively samples A, B and C, were recovered by filtration, washed with desionized water and then dried at a temperature of 60°C for 24 hours.

2.4 Preparation of bacterial growth medium

The Al-magadiite and the Cu-intercalated Al-magadiite materials (samples A, B and C) were tested on the inhibition of bacteria. A same amount (0.02 g) of these materials is deposited on the surface of solid mass PDA seeded with pure bacterial culture. Studied bacteria are *Staphylococcus aureus ATCC 25923, Escherichia coli ATCC 25922, Staphylococcus aureus ATCC 43300, Pseudomonas aeruginosa ATCC 27853* and for antifungal activity *against Candida albicans ATCC 10231* was used. 0.5 ml culture (10^8cell/ml) obtained after incubation at 37°C for 24 hours was mixed with 10 ml of medium (PDA) liquid at 40 °C. The latter, probably solid, is melted by heating and then cooled before putting in contact with the microbial suspension. The mixture was placed in Petri dishes of 90 mm. Discs materials exchanged by copper, previously sterilized at 180°C for 30 minutes, and are then deposited in the bacterial PDA medium containing the bacteria. The antimicrobial activity is determined after incubation of the dishes in an oven at 37°C for 24 h for bacteria and 48 h at 30°C for *Candida albicans*. The inhibition zone for bacterial growth was detected visually (shown later in Figure 7).

3 Results and Discussion

3.1 X-ray diffraction (XRD) analysis

The powder XRD patterns of Al-magadiite and Cu-exchanged Al-magadiite samples are shown in Fig. 1. The powder XRD pattern of Al-magadiite displayed all the reflections (*00ℓ*) corresponding to a basal spacing, d_{001}, of 15.10 Å characteristic of such a material, in good agreement with previous works [41, 49]. After exchange reactions the basal spacing d_{001} decreased from 15.10 Å to 13.65 Å, 13.72 Å and 13.30 Å for samples A, B and C prepared from $Cu(NO_3)_2$, $CuCl_2$ and $CuSO_4$, respectively. As shown in previous work, this decrease in the basal spacing is due the presence in the interlayer space of the corresponding Cu-exchanged Al-magadiite samples of non-hydrated copper ions strongly linked to the aluminosilicate layer [20]. The XRD patterns of samples A, B and C showed also the appearance of new diffraction peaks at 2θ 12.14° and 13.03° assigned to copper hydroxide phases $Cu(OH)_2$ [50, 51].

Otherwise, the reflection characteristic of layered silicate magadiite at about (25°, 2θ) still present in all exchanged samples, suggesting that the ion exchange reactions with the different sources of copper do not affect the layered structure of the Al-magadiite sample.

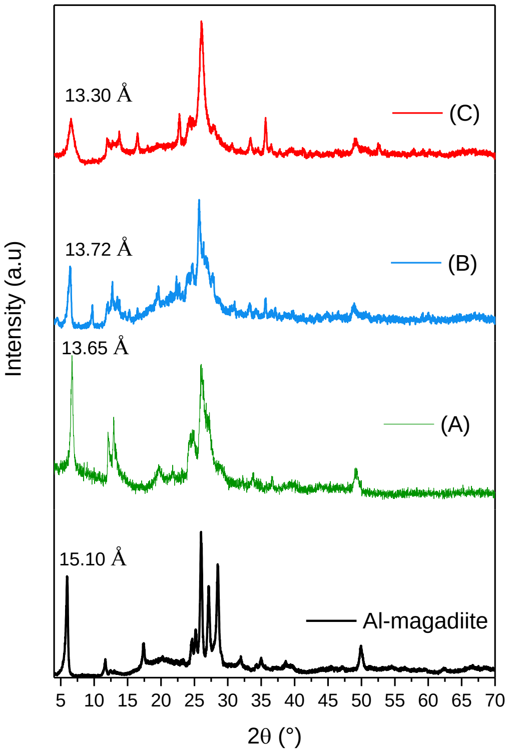

Figure 1. Powder XRD patterns of Al-magadiite and its Cu-exchanged samples A, B and C

3.2 Chemical analysis

EDS spectra of the four studied samples are shown in Fig. 2. The EDS spectrum of the as-synthesized Al-magadiite sample confirmed the presence of the elements O, Si, Na and Al located at binding energies of 0.53, 1.74, 8.04 and 1.48keV, respectively. EDS spectra of samples A, B and C showed the absence of sodium and the appearance of two additional signals attributed to copper which located at binding energies of 0.94, and 8.04 keV correspond to CuL_α and CuK_β, respectively. Indicating the presence probably of two copper species in the interlayer space of Al-magadiite. From these results, it appears that the presence of aluminum in the magadiite structure favors the total exchange of outgoing sodium ions, which is not the case for purely silicic magadiite where sodium remains in the material even for very high copper exchange rates [20].

Chemical compositions and corresponding unit cell chemical formulae of Al-magadiite and samples A, B and C were done by combining EDS and thermogravimetric (TG) analyses. The results obtained are summarized in Table 1. The chemical formula of the as-synthesized Al-magadiite sample is in good agreement with previous works, however, compared to the purely silicic magadiite, its unit cell presents an excess of sodium ions probably due to an excess of negative charges generated by the presence of tetrahedral aluminum in the structure of the silicate sheet. As shown In table 1, the exchange of ions with the copper is accompanied in all cases by a dehydration of copper-exchanged materials obtained which becomes more pronounced when the copper exchange rate increases. This result is in very good agreement with our previous work where it was shown the formation of non-hydrated copper species in the interlayer space of magadiite in which copper cations are directly and strongly bound to the ≡Si─O groups of the silicate layer [20]. Otherwise, the copper content of the sample depends on the copper salt used, ie, the nature of the counter ion and goes in the following direction: sample A> sample B> sample C. This result can probably be explained by the solubility of these salts in solution, the nitrate ion is apparently the most soluble and leads to the best result.

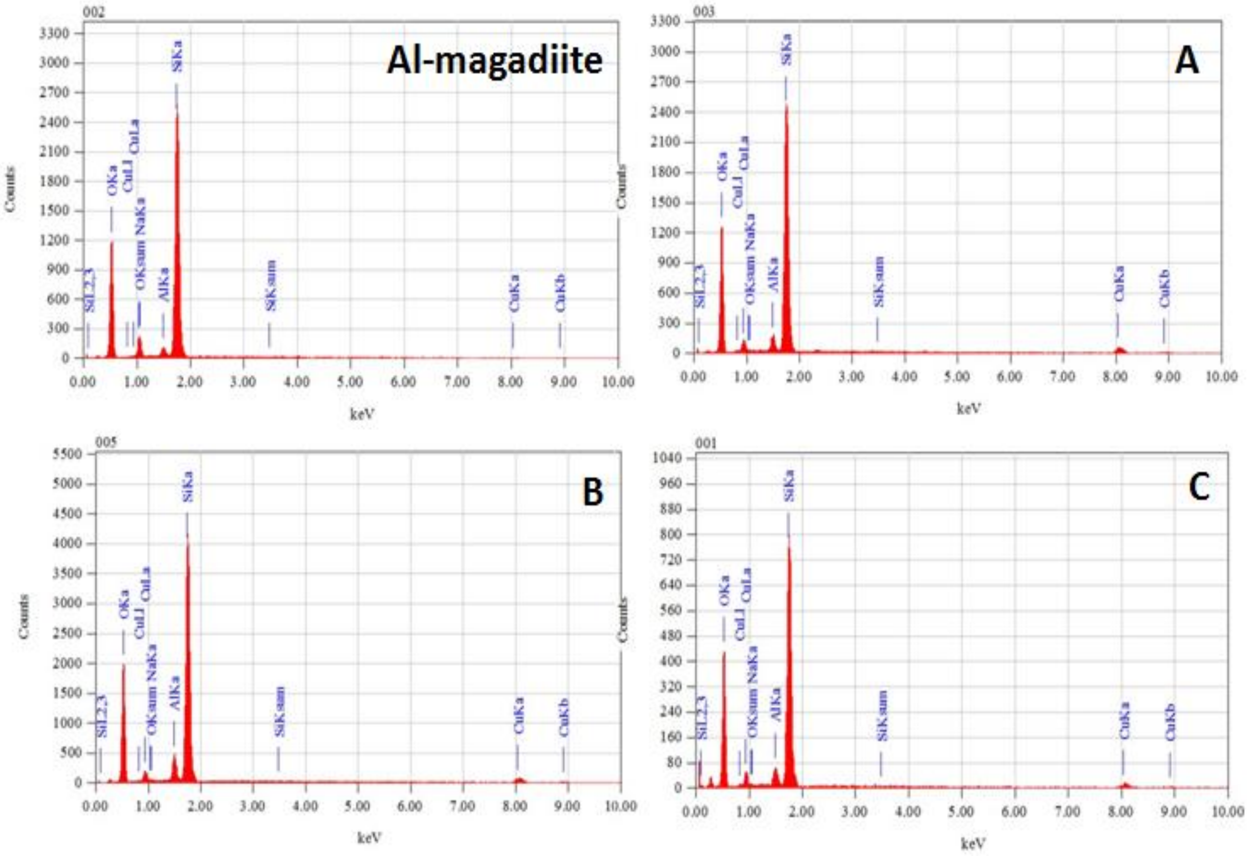

Figure 2. EDS spectra of Al-magadiite and its Cu-exchanged samples A, B and C

Figure 3 shows the scanning electron micrographs of the as-synthesized Al-magadiite material and samples A, B and C. The as-synthesized Al-magadiite sample shows a particle morphology composed of silicate layers intergrown to form spherical modules resembling rosettes characteristic of layer silicate magadiite material, which is in good correlation with previous works [19]. The diameter of a “flower” is about 9~12μm which are characteristic of layer silicate magadiite. The SEM images indicating that the product is highly crystalline [19, 52]. No impurities were detected. No significant changes in the morphologies of samples A, B and C were observed indicating that the layered structure of the starting Al-magadiite sample is preserved after ion exchange reactions.

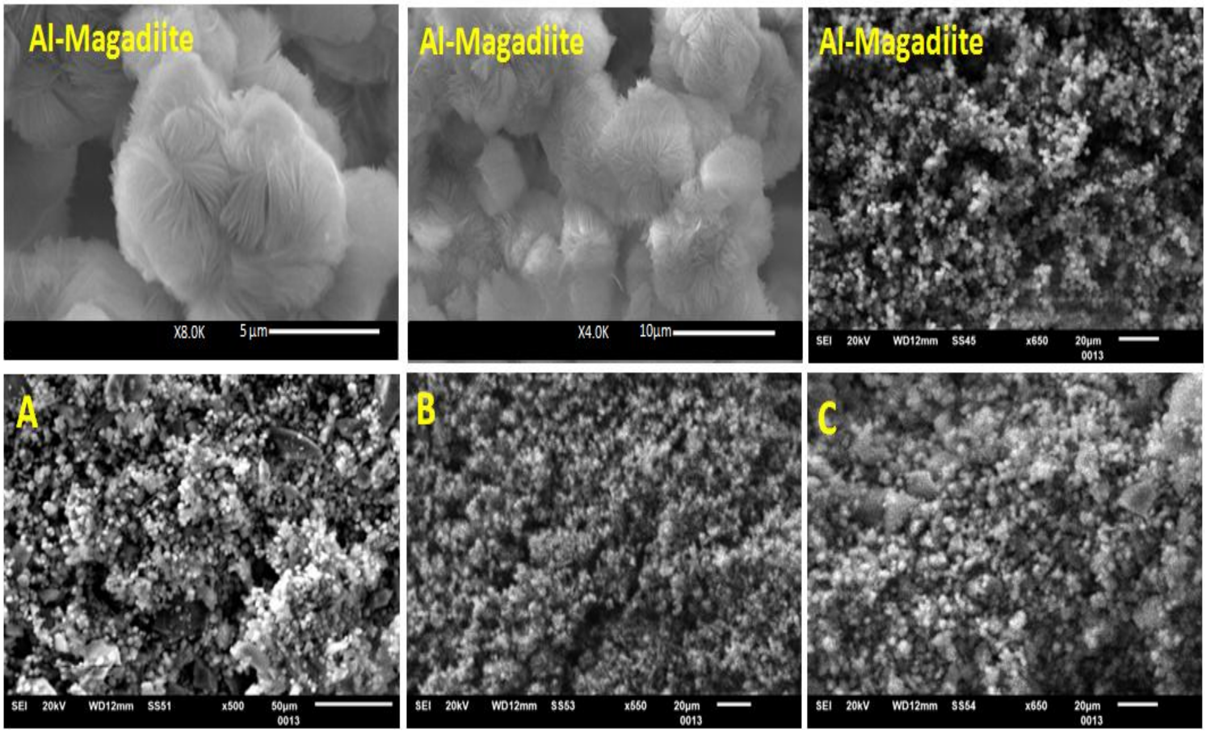

Figure 3. Scanning electron micrograph of Al-magadiite and its Cu-exchanged samples A, B and C**.**

Table 1 Chemical analysis and unit cell chemical formula of Al-magadiite and its Cu-exchanged samples A, B and C

Sample	**Atom%***					**TG (wt.%)****	**Molecular formula*****
	Si	Al	O	Na	Cu	H_2O	
Al-magadiite	28.42	0.86	65.94	4.49	-	10.56	$Na_{2.15}Si_{13.24}Al_{0.75}O_{31.52}$, $7.65H_2O$
A	28.52	1.56	67.83	-	2.09	2.50	$Cu_{0.98}Si_{13.27}Al_{0.73}O_{31.58}$, $1.81H_2O$
B	29.08	1.66	67.24	-	2.03	4.90	$Cu_{0.92}Si_{13.24}Al_{0.76}O_{30.62}$, $3.47H_2O$
C	27.27	1.69	69.69	-	1.35	6.00	$Cu_{0.65}Si_{13.18}Al_{0.82}O_{33.68}$, $4.51H_2O$

**Based on EDS results.*
***Based on TG results.*
****Molecular formulae of was calculated based on EDS and TG results.*

3.3 Fourier transforms infrared (FTIR) spectroscopy analysis

The FTIR spectra of the as-synthesized Al-magadiite samples and its copper-exchanged samples (A, B and C) are presented in Fig. 4. The Al-magadiite sample exhibited all the vibration bands characteristic of magadiite in good agreement with previous works [20, 41, 49, 53]. Indeed, the medium band at 1225 cm^{-1} is assigned to the vibration of the five membered ring groups characteristic of this material. The very strong band at 1061 cm^{-1} assigned to the vibration of interlayer $\equiv Si{-}O^-$ groups. The bands observed between 770 cm^{-1} and 500 cm^{-1} are assigned to the symmetric stretching vibration of the $\equiv Si{-}O{-}Si\equiv$ groups. The narrow absorption band at 3648 cm^{-1} is due to the presence of isolated silanol groups, $\equiv Si{-}OH$. The very broad absorption band centered at 3425 cm^{-1} is assigned to the vibrations of OH groups involved in strong interlayer hydrogen bands, $\equiv Si{-}OH{-}{-}{-}O$, as well as to the interlayer water molecules. Finally, the absorption band observed at 1625 cm^{-1} is due to the binding vibration of physisorbed water molecules. The FTIR spectra of samples A, B, and C are very similar to that of the starting Al-magadiite sample, indicating that the layered structure of these materials is preserved after ion exchange reactions. Otherwise, the appearance of a new and at 702 cm^{-1} which is reported to be absent from fully hydrated Na-magadiite indicated the formation of dehydrated Cu-exchanged Al-magadiite samples. This result is confirmed by the decrease in the intensity of the vibration bands at 1625 cm^{-1} and 3425 cm^{-1} attributed to physisorbed and intercalated water molecules, respectively.

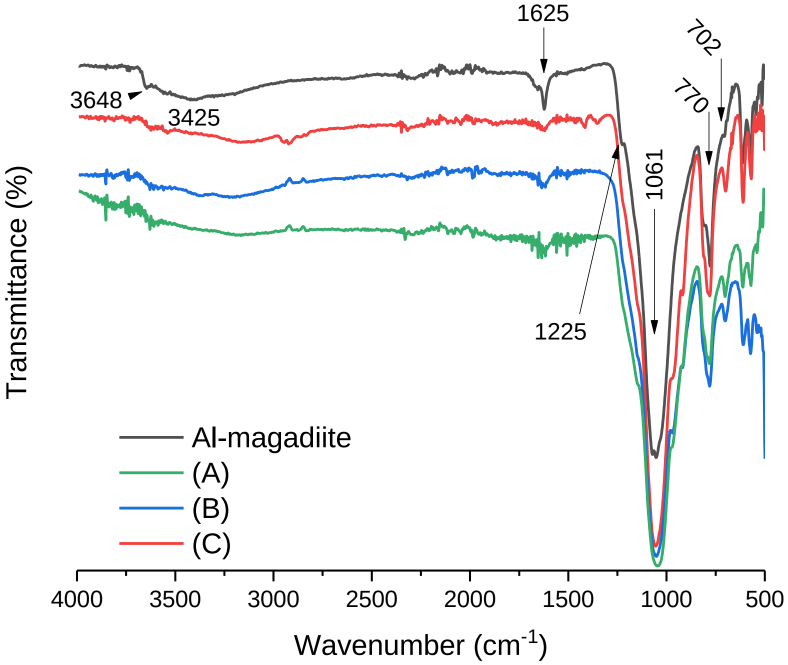

Figure 4. FTIR spectra of Al-magadiite and its Cu-exchanged samples A, B and C.

3. 4 UV–Visible diffuse reflectance (UV-Vis DR) spectroscopy analysis

The UV-Vis diffuse reflectance spectra of as-synthesized Al-magadiite and its copper-exchanged samples (A, B and C) are shown in Fig. 5. The UV-Vis diffuse reflectance spectrum showed two adsorption bands at 215 nm and 230 nm arising from the Si─O and Al─O charge-transfer of four coordinated framework silicon [20, 54] and aluminum [55, 56], respectively. Samples A, B and C show two absorption bands in UV–Vis DR spectral region between 200-1100 nm. The intensity of both these two bands is higher for sample A, prepared by exchange with copper nitrate. This may be due to the less electronegativity of the anion nitrate which can easily release the copper cation and allows magadiite to absorb more copper cations from solution. The first band observed between 220-350 nm is assigned to a charge transfer O→Cu transitions of isolated Cu^{2+} ions in coordination with lattice oxygen [57]. The second band broader and less intense observed in the UV–Vis DR spectral region between 680-800 nm is attributed to *d–d* transition of Cu^{2+}.

According to the literature, a *d–d* transition band at 750-800 nm is assigned to the Cu^{2+} in a perfect octahedral coordination [58-60]. Otherwise, these two absorption bands indicate the presence of two copper species in the interlayer space of Al-magadiite in good agreement with EDS Analysis.

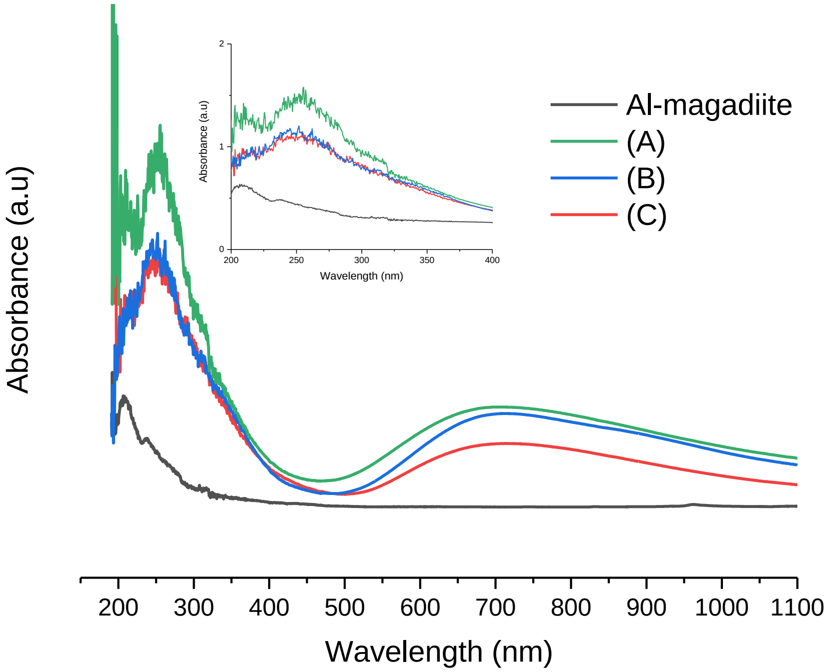

Figure 5. UV–Vis DR spectra of Al-magadiite and its Cu-exchanged samples A, B and C.

3.5 Antibacterial properties

The obtained sample Al-magadiite and Cu-exchanged Al-magadiite (A, B and C) were tested for antibacterial activity against Gram-negative (*E. coli ATCC 25922*, *P. aeruginosa ATCC 27853,*), Gram-positive (*S. aureus1 ATCC 25923, S.aureus2 ATCC 43300*) bacteria and also as *antifungal against Candida albicans* ATCC 10231. The inhibition zone for bacterial growth under and around the tested materials was observed visually Fig. 6. The data were recorded in Table 2. The Al-magadiite material shows no activity for all bacterial and fungal strains. Otherwise, samples A, B and C presented a good antibacterial activity against only Gram-positive bacteria (*S. aureus1 ATCC 25923* and *S.aureus2 ATCC 43300).* As shown in Table 2, sample A exhibits a more important inhibition zone than samples B and C. This is probably due to copper content of the sample which is more important for sample A. Thus, the copper content of the sample plays an important role in the antibacterial activity in good agreement with the literature [61]. Otherwise, the three Cu-exchanged samples (A, B and C) present a low antibacterial activity against Gram-negative bacteria *E. coli ATCC 25922*. However, no antifungal activity was observed for three studied samples.

Table 2. Halo test results of Al-magadiite and its Cu-exchanged samples A, B and C against bacterial and fungal pathogen stains

Samples	**Bacterial strains**				**Fungal strains**
	Gram-positive		**Gram-negative**		
	S. aureus1 ATCC 25923	*S.aureus2 ATCC 43300*	*E. coli ATCC 25922*	*P. aeruginosa ATCC 27853*	C. albicans ATCC 10231
Al-magadiite	NA	NA	NA	NA	NA
(A)	17mm	10mm	LO	NA	NA
(B)	16mm	13mm	LO	NA	NA
(C)	12mm	11mm	LO	NA	NA

LO: Low antibacterial activity, NA: No antibacterial Activity

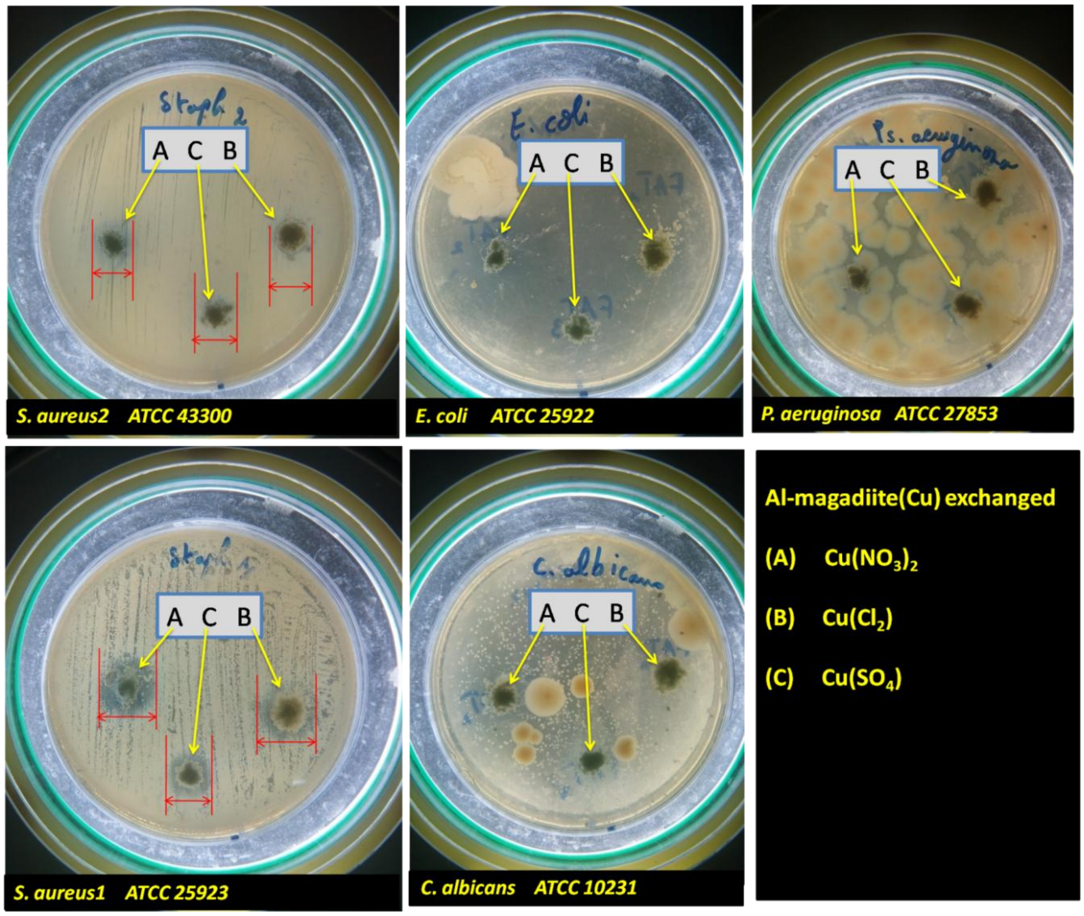

Figure 6. Inhibition zone tests of Al-magadiite and exchanged samples A, B and C against pathogen bacterial and fungal strains.

4 Conclusions

In the present work, Al-magadiite material was prepared by hydrothermal synthesis. It is then used as starting material to prepare Cu-exchanged Al-magadiite samples material using three different copper salts sources. All the materials obtained were characterized by X-ray diffraction, Fourier transforms (FTIR) spectrometer, EDS spectroscopy, scanning electron microscopy (SEM), thermogravimetric (TG) analysis and Ultraviolet-visible (UV–Vis) absorbance spectra. The results show that the as-synthesized Al-magadiite material structure contains four coordinated aluminum atoms. The presence of aluminum leads to a total exchange of the outgoing of the interlayer sodium cations. The copper exchange rate depends on the nature of counter-ions. Indeed, the best copper content was observed for the Cu-exchanged sample prepared from copper nitrate salt. Tested as antibacterial and antifungal materials against pathogen strains, all the copper exchanged materials exhibits a good antibacterial activity against Gram-positive bacteria. This activity increased with increasing the copper content of the copper exchanged sample indicating that the copper content of the sample plays an important role in the antibacterial activity in good agreement with the previous works. However, a low or no activity is observed against Gram-negative bacteria.

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