Photocatalytic remediation of methylene blue and antibacterial activity study using Schiff base-Cu complexes

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Abstract
This work describes the design of novel Cu(II) complexes and their application in the photocatalytic degradation of methylene blue (MB). The same photocatalyst exhibits antibacterial activity against Escherichia coli (gram-negative) and Bacillus circulans (gram-positive). The characterisation of the photocatalysts has been done by several up-to-date physical methods. The rationale behind the photocatalysts’ beneficial intervention is discussed in this study. Statistical analysis of the degradation of MB is done using a one-way ANOVA, and the significance of means is determined by a multiple comparison test using Turkey HSD. Also, the degradation of MB follows pseudo first-order kinetics with high correlation coefficient values ($R^2 > 0.95$), making them useful as simple and low-cost organic dye degradation agents.

Keywords Photocatalytic activity · Dye degradation · Hydrazones · Cu(II) complexes · Methylene blue · Antibacterial studies

Introduction

Organic dyes from industrial effluents can cause severe damage to the environment, leading to the destruction of the aquatic ecosystem. Moreover, they also cause water pollution and desertification and are toxic to aquatic and human lives. The textile industry, dyeing industry, paper and pulp industry, tannery, and paint industry are the major contributors of dye effluents to the environment (Robinson et al. 2001; Ghosh et al. 2019; Velusamy et al. 2021). Dyes are chemically stable, inert molecules and are resistant to the actions of sunlight, water, soap, bleach, and perspiration (Robinson et al. 2001).

The colour imparted by the dyes causes aesthetic damage to water and prevents the penetration of sunlight through water, thereby causing a considerable decrease in the rate of photosynthesis and the amount of dissolved oxygen (Roy et al. 2010). In addition to being non-biodegradable, dyes and their degradation products can be carcinogenic, mutagenic, and teratogenic and can cause long-lasting health issues (Nestmann et al. 1979; Schneider et al. 2004; Christie 2007).

Therefore, it is necessary that industrial effluents containing hazardous organic dyes be appropriately treated before being disposed of into the water resources. The properties that make the dyes useful in various applications also cause their elimination from the environment problematic. A large number of methods have been consequently developed to remove the dye pollutants from the wastewater, such as adsorption, chemical precipitation, filtration, coagulation, floatation, oxidation, ozonation, chlorination, bleaching, Fenton oxidation, ion-exchange, reverse osmosis, phytoremediation, and aerobic and anaerobic processes (Robinson et al. 2001; Tünay et al. 1996). Most of the techniques above exhibit low efficiency and require huge costs (Saratale et al. 2011; Abdelrahman et al. 2019). However, the complete degradation of organic dyes present in the effluent water using catalysts and visible light or ultraviolet radiation into innocuous products has proven to be an efficient method of effluent water treatment. This is due to the ability of this approach to degrade the organic dye molecules in a simple, environmentally benign, sustainable, and cost-effective manner (Abdelrahman et al. 2019; Jain et al. 2019). These methods mostly explored the usage of...
conventional semiconductor nanomaterials and their modifications for the photocatalytic degradation of dyes (Kang et al. 2010; Deng et al. 2017; Dong et al. 2017; Zhang et al. 2017; Sun et al. 2020).

Cu oxides sputtered on polystyrene films are reported to be excellent photocatalysts for the degradation of methylene blue under sunlight (Baghriche et al. 2017). Metal complexes are also good candidates for the photocatalytic degradation of toxic organic dyes (Qin et al. 2013; Chang et al. 2017; Roy et al. 2017; Azam et al. 2018; Wang et al. 2019a, b). There are a few reports of the use of Cu-Schiff base complexes in this regard (Wu et al. 2013; Li et al. 2014; Wang et al. 2014; Xu et al. 2015; Wu et al. 2017; Yang et al. 2018; Ghosh et al. 2019; Jain et al. 2019; Wang et al. 2019a, b; Carvalho et al. 2020; Li et al. 2020; Wang et al. 2020).

Cu-based nanocomposites are found to retain bacterial and fungal inhibition properties (Ballo et al. 2016, 2017). Numerous Cu(II) complexes have been explored for their significant antimicrobial activity (Vavříková et al. 2011). The antibacterial properties of Cu can be attributed to the destructive interaction of Cu with the bacterial cell membrane (Rtimi et al. 2020).

It would therefore be beneficial to develop copper-based complexes having a narrow bandgap that can absorb in the visible and UV region. The metal complexes reported in this work are excellent alternative to the photocatalysts based on gold, silver, ruthenium, and platinum in terms of economy. All the above reasons inspired us to synthesise three new copper (II) complexes (C1, C2, and C3) with the ligand N′-(3-hydroxy-4-methoxybenzylidene)nicotinohydrazide (HL) and explore their use as photocatalysts in the degradation of methylene blue. The degradation kinetics of methylene blue using these complexes is examined. Furthermore, the antibacterial properties of the compounds were studied against *Escherichia coli* (gram-negative) and *Bacillus circulans* (gram-positive) by the disc diffusion method.

### Materials and methods

All the chemicals and solvents were of analytical grade. Pyridine-3-carbohydrazide (Sigma Aldrich), 3-hydroxy-4-methoxy-benzaldehyde (Spectrochem), CuSO₄·5H₂O (S.D. Fine), Cu(OAc)₂·4H₂O (Merck), sodium azide (Spectrochem), glacial acetic acid, methanol, and dimethylsulfoxide were used as received.

### Synthesis of the ligand N′-(3-hydroxy-4-methoxybenzylidene)nicotinohydrazide (HL)

Pyridine-3-carbohydrazide (0.5 mmol, 0.0685 g) and 3-hydroxy-4-methoxy-benzaldehyde (0.5 mmol, 0.0761 g) were separately dissolved in minimum amount of methanol. The two solutions were mixed four drops of glacial acetic acid was added and refluxed for 2.5 h. Cooled and the resulting pale yellow solution was allowed to air dry for a few days. The ligand HL crystallised out from the mother liquor as colourless, block-shaped crystals. Filtered, washed with methanol, and dried (Scheme 1). Elemental Anal. Found (Calcd.) (%): C, 61.50 (61.99); H, 4.52 (4.83); N, 15.95 (15.49).

### Syntheses of Cu(II) complexes

#### Synthesis of [Cu(L)₂] (C1)

HL (1 mmol, 0.271 g) was dissolved in minimum amount of methanol. A solution of Cu(OAc)₂·4H₂O (0.5 mmol, 0.1278 g) dissolved in minimum amount of water was added and the reaction mixture was refluxed for 3 h. Pale
green crystalline powder obtained was filtered, washed with methanol, and dried. Elemental Anal. Found (Calcd.) (%): C, 55.85 (55.67); H, 4.65 (4.00); N, 13.55 (13.91).

**Synthesis of \([\text{Cu}_2(\text{HL})_2(N_3)_2]\) (C2)**

\(\text{HL}\) (1 mmol, 0.271 g) was dissolved in minimum amount of methanol. \(\text{Cu(OAc)}_2\cdot4\text{H}_2\text{O}\) (1 mmol, 0.2557 g) and sodium azide (1 mmol, 0.065 g) were added, mixed well, and stirred for 2 h. Dark green coloured product obtained was filtered, washed with methanol, and dried. Elemental Anal. Found (Calcd.) (%): C, 48.25 (48.73); H, 3.25 (3.80); N, 24.65 (24.35).

**Synthesis of \([\text{Cu}(\text{HL})_2(\text{SO}_4)]\) (C3)**

\(\text{HL}\) (1 mmol, 0.271 g) was dissolved in minimum amount of methanol. To this, \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\) (1 mmol, 0.1596 g) was added, mixed well, and stirred for 2 h. Green coloured product obtained was filtered, washed with methanol, and dried. Elemental Anal. Found (Calcd.) (%): C, 48.25 (47.90); H, 3.52 (3.73); N, 11.55 (11.97).

**Physical measurements**

Elemental analyses of all the compounds were done on a Vario EL III CHNS analyzer at SAIF, Kochi, India. IR spectra were recorded on a Thermo Nicolet Avatar 370 DTGS model FT-IR Spectrophotometer in the range of 4000–400 cm\(^{-1}\) using KBr pellets at SAIF, Kochi. The \(^1\)H NMR spectrum of \(\text{HL}\) was recorded using a Bruker Avance III 400 MHz FT-NMR Spectrometer with deuterated DMSO as the solvent and TMS as an internal standard at SAIF, Kochi, India. Electronic spectra in DMSO were recorded on a Shimadzu UV–Vis Double Beam in the 200–900 nm range.

**Photocatalytic dye degradation studies**

The photocatalytic dye degradation efficiency of the Schiff base Cu(II) complexes were determined by investigating the degradation of methylene blue (MB) in water as a model system. 0.035 g of the complexes were dispersed in a 15-ppm aqueous solution of MB. In order to attain the adsorption–desorption equilibrium of dye molecules over the Cu(II) catalysts, the above mixtures were stirred for 30 min in the dark. The UV–Vis absorption spectra of the mixtures were recorded. The mixtures were then stirred under a UV irradiation lamp of 25 W, and UV–Vis spectra were recorded on a half-hour basis.

The degradation efficiencies (\(D\)) for MB were calculated using the formula (Pathania et al. 2016; Azam et al. 2018; Wang et al. 2020),

\[
\% \text{ photodegradation} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100
\]

where \(A_0\) is the absorbance of MB before degradation; \(A_t\) is the absorbance of the solution after illumination at time \(t\).

According to first-order reaction kinetics, rate constant \(k\) (min\(^{-1}\)) was determined by using the following relation:

\[
\ln \left( \frac{C_t}{C_0} \right) = kt
\]

where \(C_0\) is the initial concentration and \(C_t\) is the concentration at time \(t\).

**Antibacterial studies**

The disc diffusion method was used to test the antimicrobial activity of the Schiff base \(\text{HL}\) and the three Cu(II) complexes \(\text{C1, C2,}\) and \(\text{C3}\) against two human pathogenic bacterial strains: \(\text{Escherichia coli}\) (gram-negative) and \(\text{Bacillus circulans}\) (gram-positive). All the bacterial cultures were procured from microbial culture types and sub-cultured in nutrient agar. Ciprofloxacin was used as the positive control, and DMSO was used as the negative control. 0.0001 g of the compounds was dissolved in 10 ml of DMSO, and these solutions were used for the assay.

**Results and discussion**

In the present work, we synthesised a novel Schiff base ligand, \(\text{N’-}(3\text{-hydroxy-4-methoxybenzylidene})\text{nicotinohydrazide (HL)}\) and its three Cu(II) complexes, \(\text{C1, C2,}\) and \(\text{C3}\). The compounds were characterised by elemental analyses and IR and electronic spectroscopic techniques. \(\text{HL}\) was further characterised by \(^1\)H NMR studies. The use of the Cu(II) complexes as photocatalysts for the degradation of methylene blue was investigated. Degradation kinetic studies were also performed. Moreover, all the compounds were assayed for their antibacterial activities.

**Infrared spectra**

The IR spectra of all the compounds are presented in Fig. 1. The IR spectrum of the ligand displayed a band ca. 3388 cm\(^{-1}\) due to \(\nu(\text{OH})\) phenolic stretching (Zhang et al. 2012; Sang et al. 2020). A sharp band ca. 3388 cm\(^{-1}\) can be assigned to the \(\nu(\text{NH})\) stretching (Zhang et al. 2012). The \(\nu(\text{C}=\text{O})\) of the ligand is observed as a strong and sharp band at 1655 cm\(^{-1}\). There is a medium band ca. 1597 cm\(^{-1}\) corresponding to the \(\nu(\text{C}=\text{N})\) stretching of the azomethine function in the ligand. The \(\nu(\text{N–N})\) vibration is seen ca. 1174 cm\(^{-1}\) as a medium band. All of the above indicate the existence of the ligand \(\text{HL}\) in the amido form in the solid state. The sharp and medium band ca. 1244 cm\(^{-1}\) is assigned
to the $\nu$(C–O) stretching. A weak band ca. 3040 cm$^{-1}$ is due to $\nu$(CH) aryl stretching and the medium band ca. 1380 cm$^{-1}$ may be ascribed to the symmetric bending of the methyl group in the ligand. Also, aromatic $\nu$(C = C) stretching vibration is seen as sharp peaks ca. 1540 and 1435 cm$^{-1}$.

The frequencies of absorption of the C = N bond of the azomethine group are affected by coordination to the metal centre and are shifted to lower wavenumbers attributed to the conjugation of the p-orbital on the double bond with the d-orbital on the metal ion, thereby reducing the force constant. The IR spectra of all the three Cu(II) complexes revealed a red-shifting of the band due to $\nu$(C = N) stretching by 20–84 cm$^{-1}$. Moreover, in all the complexes, the band due to $\nu$(C = O) is present, but is seen to be downshifted by 47–55 cm$^{-1}$. These two features indicate the coordination of the azomethine N and the oxygen of the carbonyl group of the ligand to the metal in the amido form, rather than enol form. The band due to $\nu$(N–N) stretching is shifted by 13–19 cm$^{-1}$ in the complexes C2 and C3. This increase in frequency is ascribed to the increase in the double bond character of the N–N bond, and this is another proof for the coordination of the azomethine N to the Cu(II) centre.

The IR spectra of C1 revealed the absence of the band due to the phenolic O–H stretching in the ligand, indicating the deprotonation of the phenolic oxygen and subsequent coordination to the Cu(II) centre. The band due to the $\nu$(N–H) stretching is masked by the broad band at 3500–3000 cm$^{-1}$, as a result of the presence of lattice
water in the complex. The presence of lattice water is also supported by the appearance of medium bands at 724 cm\(^{-1}\) and 697 cm\(^{-1}\), assigned to the rocking modes of lattice water. From the IR data, it can be said that in C1, Cu(II) is coordinated to the azomethine N, carbonyl oxygen and phenolic oxygen of the ligand.

In the IR spectrum of C2, occurrence of a sharp and strong band ca. 2069 cm\(^{-1}\), assigned to the \(\nu_{as}(N_3)\) stretching, indicates the presence of coordinated azido group in the complex. The high wavenumber for the \(\nu_{as}(N_3)\) may be due to bridging azide groups. The medium band at 1372 cm\(^{-1}\) may be assigned to the \(\nu_s(N_3)\) stretch and indicates the end-on coordination mode of bridging azide, as the symmetrical \(\nu_s(N_3)\) stretch of end-to-end azide bridge is IR inactive. The deformation mode of the azido ligand is detected as a weak band at 691 cm\(^{-1}\) (Tandon et al. 1994; Sasi et al. 2010; Diana et al. 2016). The IR data thus suggests that in C2, Cu(II) is coordinated to the azomethine N, carbonyl oxygen, and end-on bridging azide groups.

The IR spectrum of C3 exhibits three strong bands at 1278, 1110, and 1019 cm\(^{-1}\), which are assigned as the split bands of the vibration of sulphate ion (\(\nu_3\) mode). Splitting of the \(\nu_3\) mode point towards the bidentate coordination of the sulphate ion in the complex due to the lowering of symmetry from \(T_d\) to \(C_{2v}\). \(\nu_1\) and \(\nu_2\) appear as medium bands ca. 958 and 493 cm\(^{-1}\) respectively. The splitting of the \(\nu_4\) mode into three bands ca. 700–600 cm\(^{-1}\) further supports the bidentate coordination of the sulphate in the complex (Nakamoto et al. 1957). The spectrum also shows a very broad and strong band ca. 3000–3500 cm\(^{-1}\), which may be due to the phenolic O–H, and N–H stretching modes. The IR spectral data thus reveals that the Cu(II) centre is coordinated to the azomethine N, carbonyl oxygen, and bidentate sulphate groups.

**Electronic spectra**

The electronic spectra of the ligand HL and the complex C1 are shown in the Fig. S1. The \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions are
ca. 270 nm and 360 nm respectively in the ligand. The bands due to these absorptions suffered a marginal shift upon complexation of the Schiff base. The shift of the bands due to intraligand transitions is the result of the weakening of the C=N bond and extension of conjugation upon complexation. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are ca. 275 nm and 370 nm in C1 and C3 and, 275 nm and 365 nm in C2 respectively (Sheeja et al. 2021). The absorption band observed in the 550–580 nm region in all the complexes is not present in the ligand and is ascribed to the ligand to metal charge transfer (LMCT) transitions (Hathaway et al. 1970). The very low intensity bands appearing in the 705–720-nm region in all the three complexes is due to the $d-d$ transitions. The broadness of the bands does not permit its resolution. This happens because the four low-lying $d$-orbitals of the Cu(II) are very closely spaced.

$^1$H NMR spectrum of the Schiff base (HL)

The $^1$H NMR spectrum of the ligand HL is depicted in the Fig. S2. The sharp singlet at $\delta$ 11.866 ppm indicates the presence of phenolic proton. The absence of any coupling interactions by protons on neighbouring atoms renders singlet peaks for the phenolic proton. A singlet at $\delta$ 9.384 ppm is assigned to the imine NH proton. The singlet at $\delta$ 9.049 ppm is assigned to the imine proton. Aromatic protons of the pyridine ring appear at $\delta$ 8.757–7.546 ppm range and aromatic protons of the benzene ring appear at $\delta$ 7.295–6.977 ppm as multiplets. A singlet at $\delta$ 3.812 ppm corresponds to the methoxy protons.

Based on the above physicochemical studies, the following tentative structures are proposed for the Schiff base ligand HL and the Cu(II) complexes C1, C2, and C3 (Fig. 2a,b,c and d).

**Photocatalytic dye degradation**

Figure 3 shows the photocatalytic activity of complexes C1, C2, and C3, which is demonstrated using the degradation of methylene blue (MB) upon irradiation with ultra violet radiation. Figure 3a,b, and c show the decrease in intensity of the absorption peak of MB in the presence of photocatalysts C1, C2, and C3. The absorption peak of MB at 663 nm is attributed to the absorbance of the $n \rightarrow \pi^*$ transitions of the dye (Heger et al. 2005). The decolorisation of dye solutions in the presence of photocatalysts is followed by the decrease in intensity of the absorption maximum at 663 nm, which is directly related to the degree of degradation of dye. The maximum absorption of MB at 663 nm was reduced continuously in the reaction process, which revealed the destruction of the conjugated ring of MB.

**Table 1** Descriptive statistics and one-way ANOVA

| Time | Catalyst | N  | Mean   | Std. deviation | F        | Sig   |
|------|----------|----|--------|----------------|----------|-------|
| 0    | C1       | 301| .344559| .3281713       | 38.640   | $p < 0.05$ |
|      | C2       | 301| .509590| .2556510       |          |       |
|      | C3       | 301| .295855| .3466891       |          |       |
|      | Total    | 903| .383335| .3254338       |          |       |
| 30   | C1       | 301| .303688| .3015525       | 75.839   | $p < 0.05$ |
|      | C2       | 301| .550974| .2269511       |          |       |
|      | C3       | 301| .292727| .3390714       |          |       |
|      | Total    | 903| .382463| .3141511       |          |       |
| 60   | C1       | 301| .325071| .2793496       | 16.293   | $p < 0.05$ |
|      | C2       | 301| .403131| .2268734       |          |       |
|      | C3       | 301| .277685| .3047668       |          |       |
|      | Total    | 903| .335296| .2768462       |          |       |
| 90   | C1       | 301| .345985| .2423982       | 20.877   | $p < 0.05$ |
|      | C2       | 301| .270375| .2480724       |          |       |
|      | C3       | 301| .217477| .2452290       |          |       |
|      | Total    | 903| .277946| .2505902       |          |       |
| 120  | C1       | 301| .2511103| .22990122     | 3.189 | $p < 0.05$ |
|      | C2       | 301| .2089674| .23955340     |          |       |
|      | C3       | 301| .2089674| .23955340     |          |       |
|      | Total    | 903| .2330151| .2369280      |          |       |
| 150  | C1       | 301| .2214611| .18633125     | 13.480 | $p < 0.05$ |
|      | C2       | 301| .1542003| .17445992     |          |       |
|      | C3       | 301| .1567751| .17927737     |          |       |
|      | Total    | 903| .1774788| .18256363     |          |       |
The decolorisation of dye takes place in two phases. During the first phase, the catalyst and dye solution were kept in constant stirring for 30 min (in the absence of UV light) to achieve an adsorption–desorption equilibrium, and it was discovered that complex C2 has higher adsorption. In the second stage, the UV lamp was switched on and the catalyst/dye solution was irradiated using UV light. UV–vis absorption of the irradiated solution is measured at a constant interval of 30 min. The decolorisation of the dye is by adsorption in the first phase, and by the degradation of the dye in the second phase. Figure 3d shows the percentage degradation of dye as a function of time. The percentage degradation of dye using C1, C2, and C3 was found to be 50%, 52%, and 51%, respectively.

Statistical analysis of photocatalytic activity

The descriptive statistics detailed under Table 1 explains about the effect of various catalysts across different time periods. At ‘0’ time, it is found that catalyst C1 has got the best adsorption (mean 0.295, std.dev 0.346) when compared to C2 (mean 0.509, std.dev 0.255) and C3 (mean 0.295, std. dev 0.346). In order to check the significance of this finding, a one-way ANOVA test was attempted. The test was found to be significant (F = 38.640, p < 0.05), and thus, it can be proved that any one of the means are significantly different. At time, 30 min and 60 min, C1 (mean 0.304 and 0.325, std. dev 0.301 and 0.279) and C3 (mean 0.293 and 0.278, std. dev 0.334 and 0.305) show comparable catalysis efficiencies which is higher than that of C2 (mean 0.551 and 0.403, std. dev 0.227 and 0.227). However, from 90 to 120 min, the efficiency of C2 started increasing, and finally, at 150 min, it reaches maximum compared to that of C1 and C3.

Further an attempt is made to find out the significance of means by a multiple comparison test using Turkey HSD (Table 2). It is observed that at ‘0’ time level, there exists a significant difference in adsorption between C1 and C2 (mean difference −0.165, p < 0.05), C2 and C3 (mean difference 0.213, p < 0.05) but not between C1 and C3 (mean difference 0.048, p > 0.05). Hence, it can be concluded that there is no statistical evidence to believe that C1 and C3 have got difference in adsorption. Hence, the adsorption was found to be high for C1 and C3 compared to C2. Similar observation is found at 30 min and 60 min also. At 90 min, significance differences are found between the catalytic efficiencies of C1, C2, and C3. However at 120 min, no significant differences are found between the efficiencies of all the three complexes, C1, C2, and C3. Finally at 150 min, the difference in catalytic efficiencies between C1 and C2 and also, C1 and C3 are noticeable. However, that between C2 and C3 is feeble.

Mechanism for photodegradation of MB dye

Scheme 2 explains the variation in energy levels of ligands on complexation with metal. The π* orbitals are more stabilised due to the interaction between metal and ligand. The nonbonding orbital is also stabilised but not as pronounced as in π*, because of the stronger interaction between polar π* with metal. The electronic spectral data shows that all

Table 2 Multiple comparisons

| Dependent variable | (I) Catalyst | (J) Catalyst | Mean difference (I-J) | Sig |
|-------------------|--------------|--------------|-----------------------|-----|
| 0                 | C1           | C2           | −0.1650316*           | .000|
|                   | C3           |              | .0487033              | .136|
| 30                | C1           | C2           | −0.2472854*           | .000|
|                   | C3           |              | .0109618              | .889|
| 60                | C1           | C2           | −0.0780598*           | .001|
|                   | C3           |              | .0473860              | .083|
| 90                | C1           | C2           | 0.0528977*            | .023|
|                   | C3           |              | 0.1285080*            | .000|
| 120               | C1           | C2           | 0.04214286            | .074|
|                   | C3           |              | 0.04214286            | .074|
| 150               | C1           | C2           | 0.06726080*           | .000|
|                   | C3           |              | 0.06468605*           | .000|
|                   | C2           |              | 0.06726080*           | .000|
|                   | C3           |              | 0.0257475             | .983|
|                   | C1           |              | 0.06468605*           | .000|
|                   | C2           |              | 0.0257475             | .983|

*The mean difference is significant at the 0.05 level
three complexes are more or like of same state of energy levels and are of same potential for electrons and holes. This accounts for the comparable percentage of dye degradation using the three complexes, C1, C2, C3.

UV light irradiation results in the occupation of electrons in LUMO and formation of holes in HOMO. Oxidation of water takes place as the valence-band holes accept electrons and convert to OH radical. The reduction potential of electrons is sufficient for the reduction of O2 to O2− and then the conversion to OH•. OH• is a strong oxidising agent, which has the capacity to degrade MB dye to CO2 (Wang et al. 2020; Liu et al. 2022).

**Kinetics of dye degradation**

At low initial concentrations, the pseudo first-order kinetic equation given by the Langmuir–Hinshelwood model was tested. Figure 4a, b, and c display the kinetics of photodegradation of MB in the presence of C1, C2, and C3. A straight line was obtained by plotting ln(Ct/C0) vs. t, where C0 is the concentration of the MB at the inception (t=0 min), Ct is the concentration at any time t, and k is the velocity constant of the pseudo-first order reaction (Alkaykh et al. 2020). From the plots, the correlation constant for the fitted line is found to be R² > 0.95, which confirms that the photocatalytic MB dye degradation tracks first-order kinetics. A good correlation to the first-order reaction kinetics (R² = 0.9860 for C1, R² = 0.9606 for C2, and R² = 0.9618 for C3) is observed. The calculated pseudo-first-order rate constants for photocatalysis using C1, C2, and C3 are 2.63 × 10⁻³ cm⁻¹, 3.84 × 10⁻³ cm⁻¹, and 3.6 × 10⁻³ cm⁻¹, respectively. The good photo-reactivity of catalysts is confirmed by the results, which verify the corresponding degradation efficiency.

**Antibacterial studies**

The antibacterial activity of the ligand HL and the copper complexes, C1, C2, and C3, was investigated against gram-negative bacterium *E. coli* and gram-positive bacterium *B. circulans* by disc diffusion method. The diameters of the
Table 3  Zone of inhibition (in mm) of ligand HL and copper complexes C1, C2, and C3 against E. coli and B. circulans

| Compound | Zone of inhibition (mm) |
|----------|-------------------------|
| E. coli  | B. circulans             |
| HL       | 1.9                     | -                        |
| C1       | -                       | 1.5                      |
| C2       | -                       | 1.7                      |
| C3       | -                       | 1.8                      |

zones of inhibition are given in Table 3. The positive control Ciprofloxacin produced a zone of inhibition of 25 mm, and the negative control showed no inhibition for the bacteria. The Schiff base was less sensitive against E. coli, and inactive against B. circulans. However, upon complexation, a reversal of the activity is observed. All the complexes were inactive against E. coli and active against B. circulans. Complex C3 was found to exhibit maximum activity against B. circulans. A comparison of the zones of inhibition of HL and the complexes reveals a decrease in the antimicrobial activity in the metal complexes than the ligand for gram-negative bacterium, and an increase in the antimicrobial activity in the metal complexes than the ligand for gram-positive bacteria (Ramadan 1997) (Fig. 5).

Conclusion

In summary, three Cu(II) complexes (C1, C2, C3) with the ligand N′-(3-hydroxy-4-methoxybenzylidene)nicotinohydrazide (HL) were synthesised via a simple synthetic strategy, and the compounds were characterised by elemental analyses, IR, and electronic spectroscopic techniques. HL
was further characterised by $^1$H NMR studies. MB dye degradation experiments confirmed that the Cu(II) complexes exhibit significant photocatalytic activity under the irradiation of UV light. Statistical analysis of the dye degradation was carried out using a one-way ANOVA, and the significance of means was determined by a multiple comparison test using Turkey HSD. Thus, they are worthy candidates for industrial effluent treatment to eliminate organic pollutants that endanger the environment. The reuse of photocatalyst, optimisation of photodegradation in terms of pH of dye solution, intensity of UV light, etc. are being investigated. The compounds were also investigated for their antibacterial activity, and all three complexes are found to be effective against the gram-positive bacterium *B. circulans*.

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**Declarations**

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