RESEARCH ARTICLE

SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, PHOTOCATALYTIC AND ANTI-BACTERIAL ACTIVITIES OF TRANSITION METAL COMPLEXES OF FLAVONOL BASE LIGAND

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ABSTRACT

Visible light active TiO_2 nanoparticles modified with Chloro flavonol base - copper complex (Cu-CLF-TiO_2) has been prepared by chemical impregnation route. The optical properties, phase structures and morphologies of the as-prepared nanoparticles were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction(XRD). Compared to bare TiO_2, surface modified photocatalysts (Cu-CLF-TiO_2) showed are shifted in the visible region. The photocatalytic activity was monitored in the degradation of Methylene Blue (MB) dye and the results revealed that Cu-CLF-TiO_2 showed best photocatalytic activity than TiO_2. The superior photocatalytic activity of Cu-CLF-TiO_2 could be attributed to the effective electron-hole separation by the surface modifiers. The effect of photocatalyst amount, initial dye concentration and Kinetic studies on the photocatalytic activity was explained in detail. Furthermore, the antifungal activity and their usability of Cu-CLF-TiO_2 were tested.

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INTRODUCTION

A large number of Schiff bases and their metal complexes have been investigated for their interesting and important class of compounds in medicinal and pharmaceutical field. They show biological applications including anti-bacterial (Zhang, 2009; Wang, 2009), anti-fungal (Zhang, 2011) and anti-tumour activity (8). The co-ordination chemistry of Chloro flavonol ligand and their metal complexes involving oxygen and nitrogen donor atoms has excited great interest among chemists in recent years due to their applications in catalysis and their relevance to photocatalytic systems (Lü, 2010). Metal complexes derived from 2-(4-chlorophenyl)-3-hydroxy-4H-chromen-4-one can specially have a variety of application in spectral and biological are as (Hong, 2011; Nair, 2011). Schiff bases have been used extensively as ligands in the field of coordination chemistry; some of the reasons are that the intramolecular hydrogen bonds between the hydroxyl(O) and the imine(N) atoms which play an important role in the formation of metal complexes (Capinera, 2000; Mukherjee , 2011) Schiff base ligands may act as bidentate NO, tridentate NO_2, N_2O, and tetra dentate N_2O_2 which can be designed to yield mono nuclear, binuclear, one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) metal-organic frameworks (Kumar Maji, 2011; Chu, 2011).

Every day, lot of harmful organic pollutants are discharged into the environment from various industries (Capinera, 2000; Mukherjee , 2011). Among them, organic dyes play a vital role due to their great demand in textile, paper and printing industries. Methylene blue (MB) is a heterocyclic organic dye, frequently used in textile, cosmetic, and pharmaceutical industries. MB can cause permanent injury to humans and animals on inhalation and ingestion and the risk of the presence of this dye in water may be arisen from the burning effect of eye, nausea, vomiting and diarrhea (Kumar Maji, 2011). In recent years, some authors have reported the photo degradation of MB (Mukherjee, 2011; Kumar Maji, 2011). TiO_2 is a kind of n-type semi conductor and gained much response in the photocatalytic degradation of dyes for the past few year so wing to its non-toxicity and low cost (Chu, 2011; Zhang, 2011). Nevertheless, the wide bandgap of TiO2 hampers its photocatalytic activity under visible light, which constitutes more than 50 % of solar spectrum. Recently, K.Wangetal (2009) have studied the photocatalytic activity of silver loaded ZnO/TiO_2 photocatalyst for the degradation of methyl orange under UV irradiation and they have reported that the photocatalytic activity of the metal oxide nanocomposite was greatly improved after modified with metal complex. H.Zhang and C.Hu (7) have evaluated the effective solar absorption and radial micro channels of TiO_2

hierarchical structure for the degradation of rhodamine B and methyl orange under simulated sunlight irradiation. In our previous study, we have reported the photocatalytic activity of a flavonoid (hesperidin) modified TiO_2 nanoparticles towards the degradation of methylene blue dye in aqueous solution (Vignesh, 2012). We have observed that the photocatalytic activity of TiO_2 is significantly enhanced when modified with hesperidin. This stimulated us to study the photocatalytic activity of Schiff base – copper complex modified with TiO_2 nano particles. In this chapter, the synthesis, characterization, photocatalytic and antifungal activities of Cu-CLF-TiO_2 was investigated.

Experimental sections

MATERIALS AND METHODS

Physical methods such as elemental analysis, UV-vis., FT-IR,1H-NMR, (Yang, 2008) C-NMR, ESI-MS, UV-vis-DRS, XRD, TEM, electro chemical measurements, molar conductance, photocatalytic activity, anti-bacterial activity and kinetic studies etc.,

Synthesis of flavonol base ligand (CL-F): Reaction of an alcoholic solution of **1** with various substituted benzaldehyde / heterocyclic aldehyde in the presence of catalytic amount of Chlorobezaldehyde resulted in the formation 2-(4-chlorophenyl)-3-hydroxy-4H-chromen-4-one, which on refluxing with an aq.alcoholic solution of hydroxylamine hydrochloride in the presence of anhydrous sodium acetate furnished 2-(4-chlorophenyl) -3-hydroxy- 4H- chromen -4-one,

Scheme 1. Synthesis of 2-(4-chlorophenyl)-3-hydroxy-4H-chromen-4-one (Cl-F) and Metal complex. Ligand (Cl-F): 2-(4-chlorophenyl)-3-hydroxy-4H-chromen-4-one,60e. mp., 197 - 198°C (aq. ethanol) yield: 95%. UV λ_{max} 284, 331 nm, λmax (MeOH+AlCl$_3$): 288, 381 nm.IR (KBr, cm^{-1}):3094(3-OH), 1654 (C=O), 1611, 1586, 1555. ^{1}H NMR (500 MH$_Z$, CDCl$_3$): δ 7.3-8.1(m, 8H, Ar-H),10.5 (s, H, 3-OH).^{13}C NMR (125 MHz,CDCl$_3$):δ115.6, 120.6, 127.8, 128.8, 128.4, 135.2, 135.3, 136.9, 145.6, 157.1, 158.9,171.7 (CO). DEPT-135: δ 115.6($\uparrow$), 127.8($\uparrow$), 128.8($\uparrow$), 128.4($\uparrow$), 135.2($\uparrow$), 135.3($\uparrow$). *Anal.Calcd for* $C_{15}H_9ClO_3$: C 66.07%; H 3.33%, found: C 66.11%; H .35%.

Synthesis of Cu-CL-TiO$_2$: Cu-CL-TiO_2 was prepared by the chemical impregnation method (9) as follows: 0.005 g of Cu-CL and 2 g of TiO_2 was dispersed in 50ml of CHCl$_3$ and then the suspension was stirred at room temperature for 5h. After that the mixture was filtered, dried in an oven at 200˚C for 2h followed by calcination at 700˚Cfor 3h.

Measurement of Antibacterial activity: The antibacterial activity of the extract of compounds was determined using the well diffusion method. It was performed by sterilizing Mueller Hinton agar media. After solidification, wells were cut on the Mueller Hinton agar using cork borer. The test bacterial pathogens were swabbed onto the surface of Mueller Hinton agar plates. Wells were impregnated with 25 µl of the test samples. The plates were incubated for 30 min to allow the extract to diffuse into the medium. The plates were incubated at 30°C for 24 hours, and then the diameters of the zone of inhibition were measured in millimeters. Each antibacterial

assay was performed in triplicate and mean values were reported.

RESULTS AND DISCUSSION

XRD: The XRD patterns of TiO_2, and Cu-CLF-TiO_2 are shown in Fig.2.
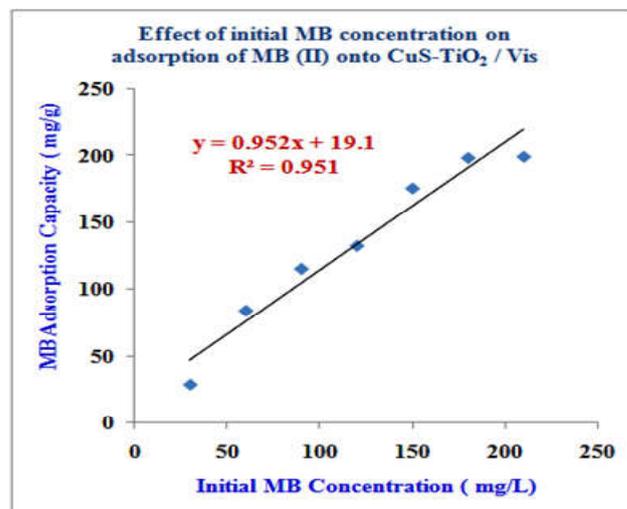

Fig. 3. Effect of concentration on the removal of MB from aqueous solution
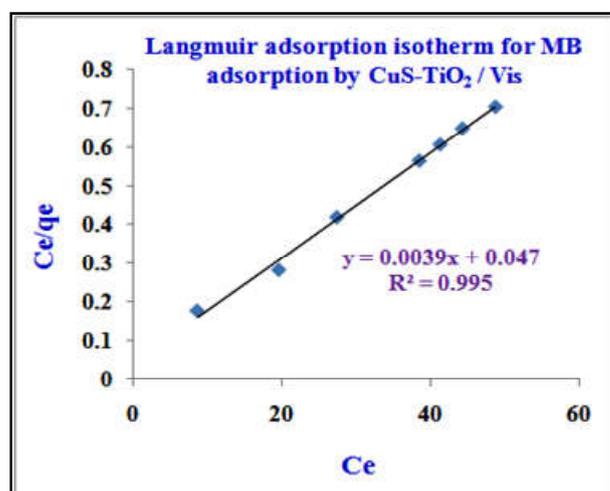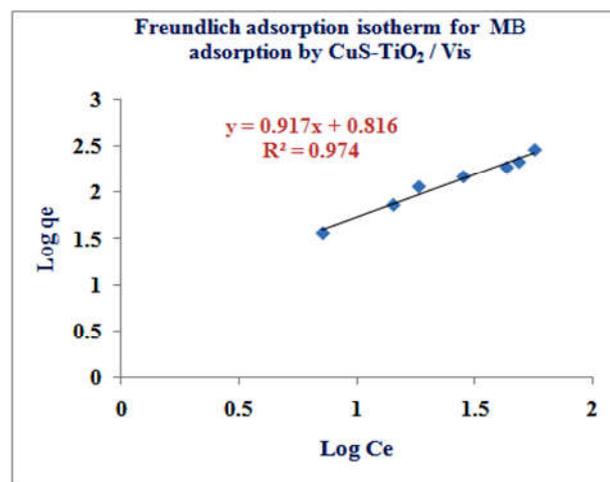

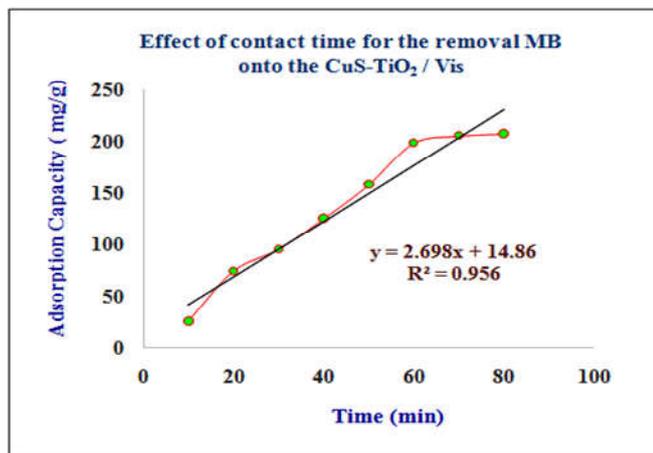**Fig.4. (a) & (b) Freundlich & Langmuir plots for the MB removal**

Fig. 5. Effect of contact time on the removal of MB from aqueous solution
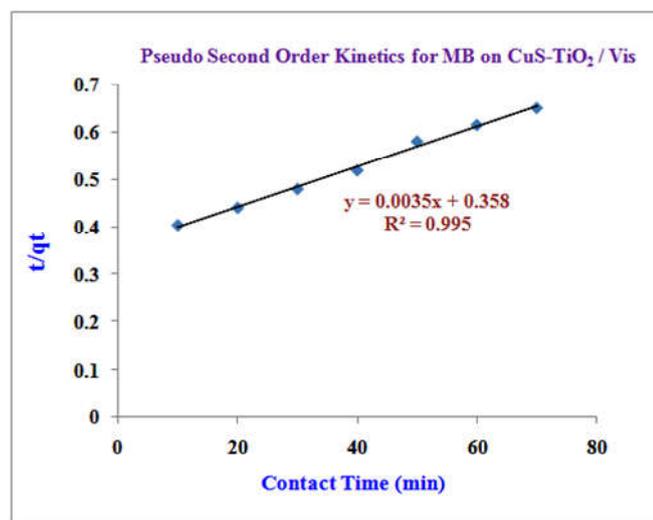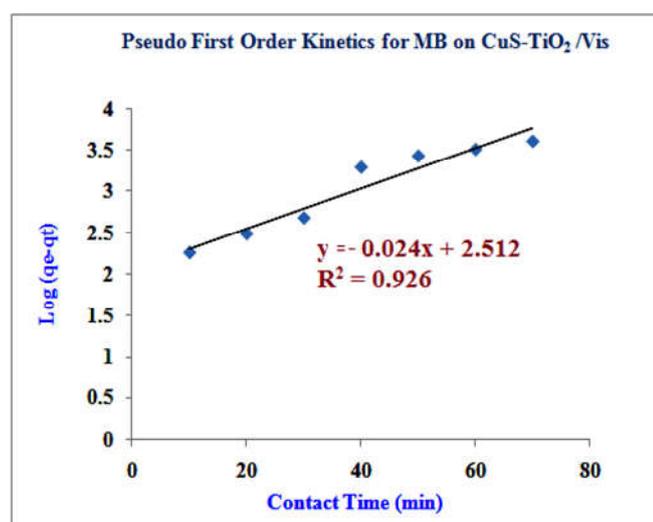

Fig.6 (a) & (b) Pseudo first and Pseudo second orderplots for MB removal

All the diffraction peaks of the samples are perfectly indexed with tetragonal phase of anatase type TiO_2 (JCPDS no. 41-1445) and the absence of other peaks indicating the high purity of TiO_2. The diffraction peaks for Cu-CLF-TiO_2 appeared to be the same as that of TiO_2, but the peak intensities are found to be significantly reduced Cu-CLF-TiO_2. This suggests those Copper complexes are dispersed well on to the surface of TiO_2.

The average crystallite sizes are calculated from the diffraction of peak broadening using the Debye-Scherer equation (Krishnan, 2009). The average crystallite sizes of TiO_2 and Cu-CLF-TiO_2 are 13.92 nm and 21.04 nm respectively. The crystallite sizes of Cu-CLF-TiO_2 are found to be higher than that of TiO_2. Therefore the surface modifiers (Cu-ClF) successfully placed on the surface of TiO_2, which alters the crystallinity without destroying the crystal structure.

Adsorption isotherm study: Fig.3 indicated clearly that the adsorption of MB onto the Cu-CLF-TiO_2 has been increased with rise in the initial dye concentration in the range 30 to 210 mg L^{-1}. The escalation in adsorption capacity with a rise in initial MB dye concentration as a import of the increase in driving force due to concentration gradient developed between the bulk solution and surface of the CuS-TiO_2. As an outcome the built-up Cu-CLF-TiO_2 can be proficiently used for the removal of high concentration MB from aqueous solution. The attraction between Cu-CLF-TiO_2 and dye can be determined with the different adsorption isotherm models. The calculated equilibrium data from the adsorption of MB onto the Cu-CLF-TiO_2 opted to the linear equation of Langmuir and Freundlich isotherm models. The linear equation for Langmuir and Freundlich isotherm models are directed as follows:

Freundlich isotherm: $\log q_e = \log K_F + (1 / n) \log C_e$

Langmuir isotherm: $(C_e / q_e) = (1 / Q_o b) + (C_e / Q_o)$

Where K_F (mg g^{-1}) is the Freundlich constant and 'n' the freundlich exponent. Where q_e (mg g^{-1}) is the adsorbed amount of MB at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of MB, Q_o (mgg^{-1}), b (L mg^{-1}) are Langmuir constants related to adsorption capacity and energy of adsorption. Added, the vital characteristics of the Langmuir isotherm can be described separation factor R_L, which is found by the equation.

$R_L = 1 / (1 + bQ_o)$

The all values are calculated from Fig.4a & b and reported in Table 1. Langmuir isotherm model for the MB adsorption was best suitable in comparison with other isotherm model by considered R^2 value. The n value was 1.0905 telling that Cu-CLF-TiO_2 is grander adsorbent for the removal of MB from aqueous solution. The R_L value range from 0 to 1 (0.0448) which approved that the adsorption process is favourable for the Cu-CLF-TiO_2 adsorbent. Former reports for the MB adsorption are comparable to the reported adsorbent. The adsorption capacity of the Cu-CLF-TiO_2 /ViS adsorbent is greater than the other reported adsorbents in the literature.

Adsorption kinetics study: Fig.5 pointed out obviously that the adsorption of MB from aqueous solution onto the Cu-CLF-TiO_2 / ViS was quick at begin of reaction and then the rate of adsorption turn into gradually down. The most sympathetic time was found for this adsorption within 60 min and beyond that no substantial change was noticed. As an upshot the equilibrium time was 60 min. The purpose for quick adsorption at commence due to the may be more available active sites in the Cu-CLF-TiO_2 / ViS for adsorption. Then and there again the more active sites may not be available in the Cu-CLF-TiO_2 / ViS for further dye molecules adsorption with effort of contact time.

Table 1. Adsorption isotherm parameters

Dye	Langmuir				Freundlich		
	Q_o(mg/g)	b (g/l)	$R_L=1/1+Q_ob$	R^2	n	K_F	R^2
MB	256.41	0.0829	0.0448	0.995	1.0905	6.5463	0.974

Table 2. Kinetic parameters

Dye	Experimental q_e (mg/g)	Pseudo-I Order Constants			Pseudo-II-Order constants		
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
MB	256.41	325.08	0.0552	0.926	285.71	4.38×10^{-6}	0.995

Table 3. Antimicrobial activity of the Copper compounds against bacterial pathogens

Test organisms	Zone of inhibition in millimeter (in diameter)			
	CuL2	L2	Solvent control	Standard Amp10µg
Escherichia coli	19	17	NZ	15
Bacillus sp	17	18	NZ	19

Plate: 1. Antimicrobial activity of Copper complex treated against *Escherichiacoli*

Plate: 2. Antimicrobial activity of ligand treated against *Escherichiacoli*

Plate 3. Antimicrobial activity of Copper complex treated against *Bacillus sp*

Plate 4. Antimicrobial activity of ligand treated against *Bacillus sp*

The rate constants were calculated with pseudo-first and pseudo-second-order kinetic models. These all kinetic models can be directed as:

Pseudo first order: $\log (q_e - q_t) = \log q_e - (k_1 / 2.303) \, t$

Pseudo second order: $t / q_t = 1/ k_2 \, q_e^2 + t/q_e$

The all values were calculated from Fig.6a & b. The calculated all values are tabulated in table 2. The R^2 value for pseudo second-order kinetic model is moderately grander to the other kinetic models. Subsequently the experimental qe value is enormously close up to the calculated qe value for pseudo-second-order kinetic model. Consequently the adsorption of MB onto the Cu-CLF-TiO$_2$ / ViS assumed with second order model kinetic model.

Antibacterial activity of Copper compounds against bacterial pathogens using well diffusion method: Antibacterial activity of the extract of compounds was determined using well diffusion method. It was performed by sterilizing Mueller Hinton agar media. After solidification, wells were cut on the Mueller Hinton agar using cork borer. The test bacterial pathogens were swabbed onto the surface of Mueller Hinton agar plates. Wells were impregnated with 25 μl of the test samples. The plates were incubated for 30 min to allow the extract to diffuse into the medium. The plates were incubated at 30°C for 24 hours, and then the diameters of the zone of inhibition were measured in millimeters. Each antibacterial assay was performed in triplicate and mean values were reported.

Standard used: Ampicillin 10μg.

Conclusion

A nano crystal line visible light sensitive Cu-Cl-F-TiO$_2$ is successfully synthesized by a simple chemical impregnation method. XRD and TEM results revealed that the crystal structure and morphology is not affected by the surface modifiers (Cu-Cl-F). Cu-Cl-F-TiO$_2$ is found to be more efficient photocatalyst for the degradation MB under visible light than Cu-Cl-F-TiO$_2$. The enhanced photocatalytic activity of Cu-Cl-F-TiO$_2$ is due to the suppression of electron-hole recombination by Cu-Cl-F-TiO$_2$.

The possible mechanism for the photo degradation of MB was also discussed in detail. The reaction conditions are optimized and maximum photo degradation is achieved within 150 min with a Cu-Cl-F-TiO$_2$ dosage of 0.2g/L and MB concentration of 8μM. In addition to that the photocatalyst (Cu-Cl-F-TiO$_2$) is found to be stable without loss of its activity after 4 cyclic experiments and it is confirmed by XRD. All the three synthe sized photocatalysts displayed better antifungal activity against *Candidaalbicans*.

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