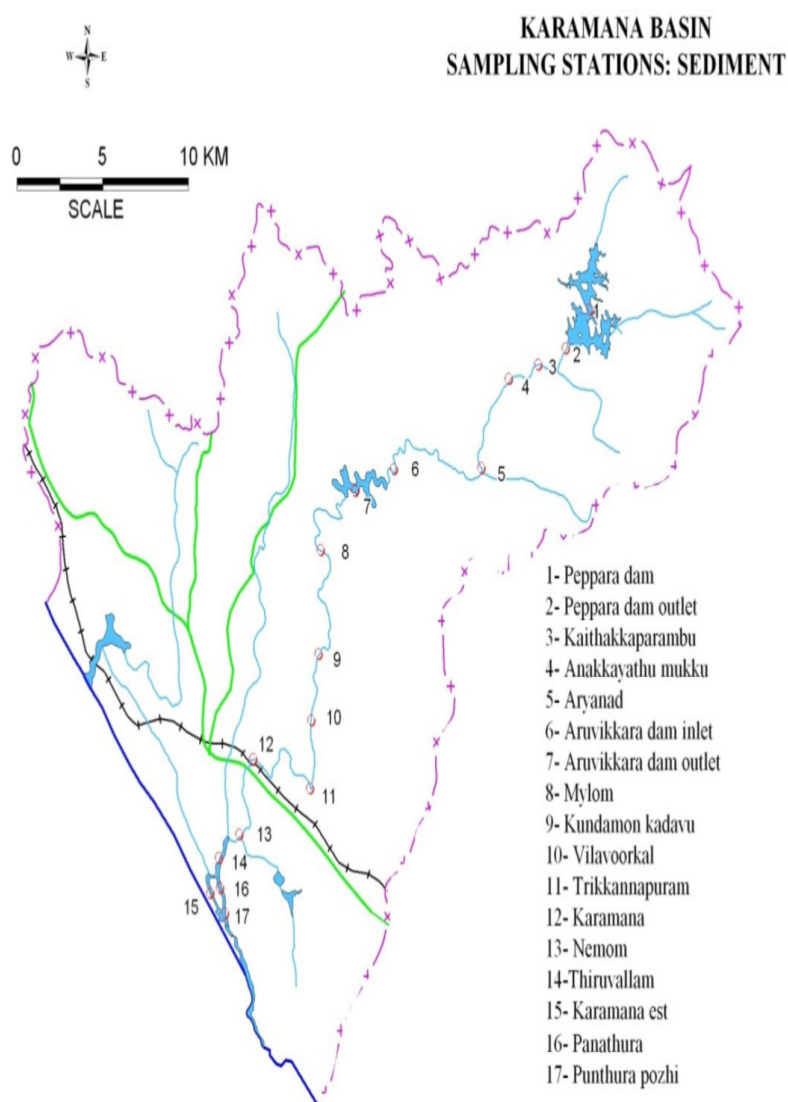




JOURNAL OF THE ACADEMY OF CHEMISTRY TEACHERS

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Effect of Method of Synthesis on the Development of Metal Organic Frameworks of Transition Metal Ions

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Abstract

Nanocrystalline and photoluminescent metal organic frameworks of zinc, cadmium and silver ions with 1,4-benzenedicarboxylic acid have been synthesized using microwave as well as hydrothermal synthetic approach. The MOFs have been characterized using FT-IR, PXRD, SEM-EDS and photoluminescence studies. The morphology depends on the method of synthesis.

Keywords: Metal organic frameworks, microwave synthesis, hydrothermal synthesis, nanocrystalline, photoluminescent

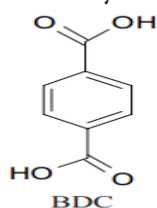
Introduction

Metal organic frameworks (MOFs), a new class of crystalline and highly porous materials have been extensively developed for a variety of applications such as gas storage and separation, luminescent materials, sensors, magnetic materials and catalysts (1-5).

In this article MOFs of transition metal ions such as Zn(II), Cd(II) and Ag(II) with 1,4-benzenedicarboxylic acid (BDC) as the organic ligand have been synthesized using two different synthetic approaches, namely, hydrothermal and microwave approaches.

Materials used

A.R quality zinc nitrate, cadmium chloride and silver nitrate were used for the present investigation. 1,4-Benzenedicarboxylic acid (terephthalic acid) was used as the organic linker in the present study.



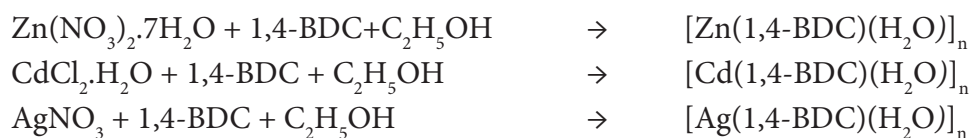
Ligand: 1,4- Benzenedicarboxylic acid (BDC)

Ethanol was used as the solvent for the preparation of metal organic frameworks.

Method of synthesis of MOFs

The MOFs have been prepared using Scheme 3.1. MOFs of zinc, silver and cadmium with 1,4-benzenedicarboxylic acid were synthesized under solvothermal conditions by the reaction of 1,4 -benzenedicarboxylic acid (BDC) with corresponding metal salts in 1:1 ratio. 1mmol of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ or AgNO_3 was mixed with 1mmol of BDC using 10ml of ethanol as the solvent. The reaction mixture was transferred to a Teflon lined autoclave. The reaction was carried out at 150°C for 3 days under autogeneous pressure and cooled afterwards to get crystals. The crystals were filtered off, washed thoroughly with ethanol and dried at room temperature.

In microwave condition, the metal salts and ligand are taken in 1:1 ratio with ethanol (10ml) as the solvent. The mixture is then transferred to a 100ml conical flask, sealed and placed inside the house hold microwave oven at 800W for 30 minutes. The crystals were washed with ethanol and dried at room temperature.



Scheme 3.1.

Experimental

The IR spectrum of the sample was recorded on SCHIMADZU DR 43 S Spectrometer using KBr pellets in the range of 400-5000 cm^{-1} . X-ray powder diffraction pattern of the MOF compound was recorded on Bruker D8 Advance X-ray diffractometer using Cu $\text{K}\alpha$ radiation = 1.5406 Å. SEM analyses of the compounds were done using FEI Nova Nano SEM 450. Elemental analyses of the compounds using energy dispersion spectroscopy were determined by Bruker Xflash 6/10. The photoluminescence (PL) spectra were recorded on a Spex-Fluorolog FL22 Spectrofluorimeter equipped with a double grating 0.22 m Spex 1680 monochromator and a 450W Xe lamp as the excitation source operating in the front face mode.

Results and Discussion

The synthesized MOFs have been characterized using FT-IR, powder XRD, SEM-EDS analysis and photoluminescence studies. The IR spectra of ligand as well as MOFs of Zn, Cd and Ag, synthesized by both microwave and hydrothermal methods are shown in figures 1 to 7. The shifts in the frequencies corresponding to the $-\text{COO}$ group in the ligand and in MOFs indicate the interaction of COO group in the MOF formation. There is a slight variation in the frequencies observed in the case of MOFs synthesized by different methods. Table 1 depicts the IR spectral data of all these MOFs.

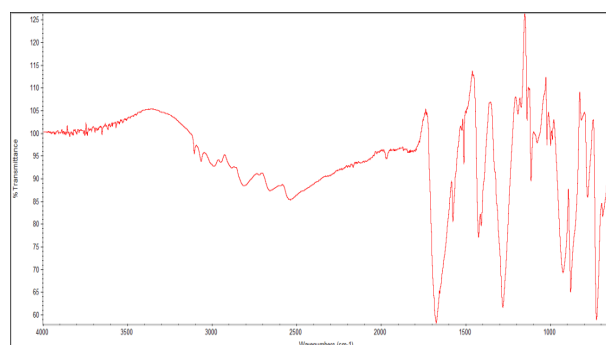


Fig.1. FTIR spectrum of 1,4-BDC

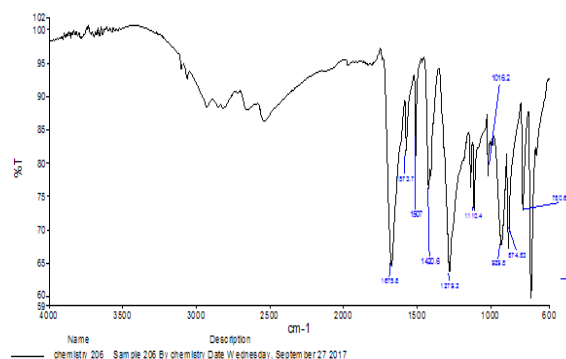


Fig.2. FT-IR spectrum of Zn-BDC MOF (solvothetical method)

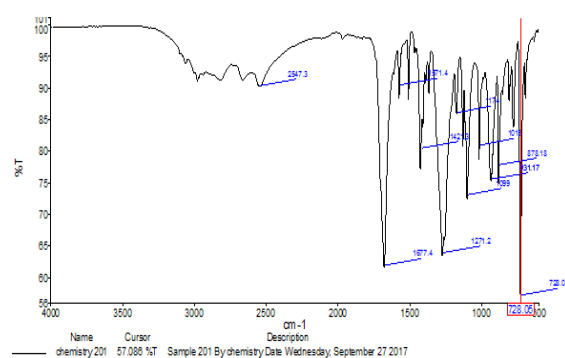


Fig.3. FT-IR spectrum of Zn-BDC MOF (microwave method)

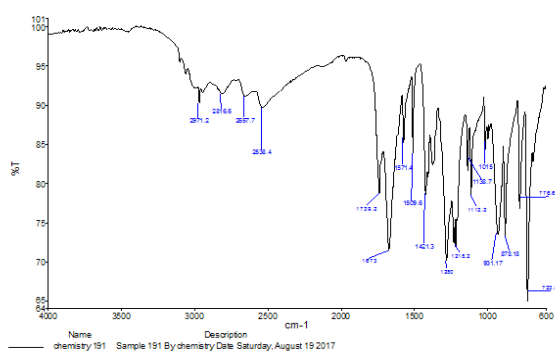


Fig.4. FT-IR spectrum of Cd-BDC MOF (solvothetical method)

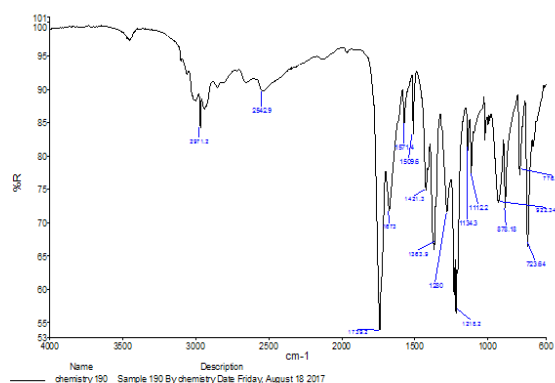


Fig.5. FT-IR spectrum of Cd-BDC MOF (microwave method)

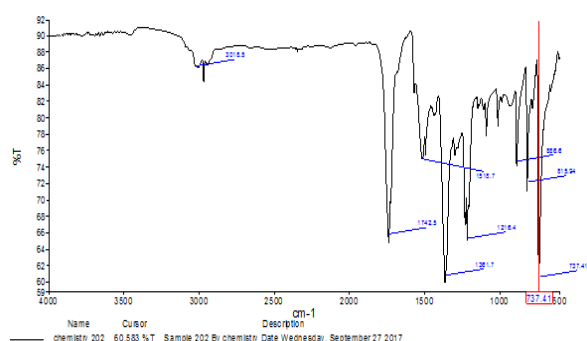


Fig.6. FTIR spectrum of Ag-BDC MOF (solvothermal method)

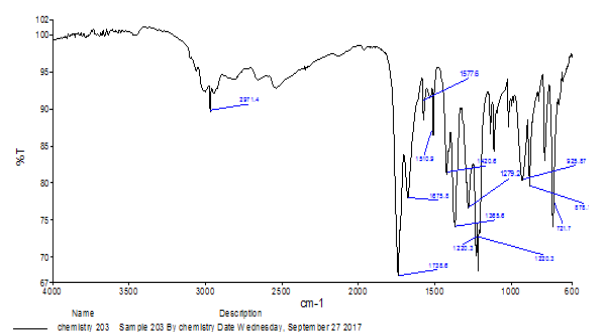


Fig.7. FTIR spectrum of Ag-BDC MOF (microwave method)

Powder XRD Analysis

The PXRD pattern of the various metal organic frameworks is shown in Figs. 8-13. The sharp peaks of PXRD pattern show that MOFs are crystalline in nature. Using Debye-Scherrer equation ($D = K\lambda/\beta\cos\theta$) average crystalline sizes are calculated. The data show that the frameworks are of nanosizes.

In the PXRD of Zn-BDC MOF, synthesized by solvothermal method, the high intensity Bragg diffraction peaks are observed at $2\theta = 13.52, 18.13, 22.42, 28.55,$ and 31.32° . The average grain size is calculated as 3.81 nm and is found to be nano sized (Fig.8).

Table 1. Infrared spectral data of MOFs

LIGAND cm ⁻¹	Zn-BDC (solvo) cm ⁻¹	Zn-BDC (micro) cm ⁻¹	Cd-BDC (solvo) cm ⁻¹	Cd-BDC (micro) cm ⁻¹	Ag-BDC (solvo) cm ⁻¹	Ag-BDC (micro) cm ⁻¹	ASSIGNMENT
1673	1675	1677	1729	1739, 1672	1742	1726, 1675	-COOH stretching
3200-2800	2998	2547	2971-2538	2971-2542	2971-2542	2971	-OH stretch of COOH
1500-1400	1507-1420	1571-1421	1571-1509	1571-1509	1518.7	1577-1420	Symmetric & Asymmetric Stretching of CO bond
1150-800	929-874	1174-831	1112-878	1262-1112	1216.4 - 838.6	1220-925	Symmetric & Asymmetric Stretching of COO bond
-	750	728	776-722	776-723	813-727.	721	Ring in & out of plane Bending vibrations

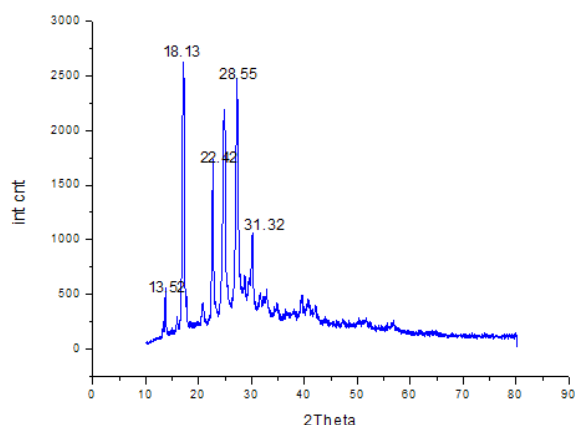


Fig.8. Powder XRD pattern of Zn-BDC MOF (solvothermal method)

In the PXRD of Zn –BDC MOF, synthesized by microwave method, the high intensity Bragg diffraction peaks are observed at $2\theta = 14.74, 16.29, 19.97, 22.12, 28.55,$ and 40.22° . The average grain sizes is calculated as 4.78 nm and is nano sized (Fig.9).

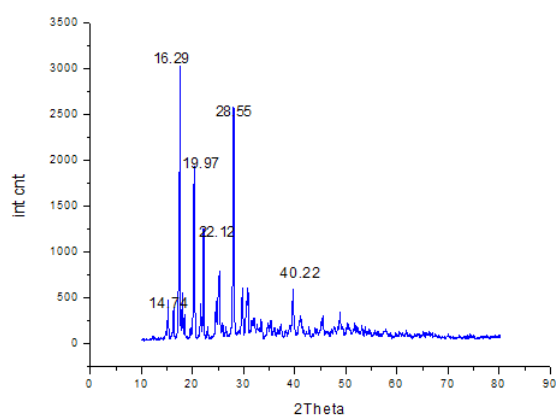


Fig.9. Powder XRD pattern of Zn-BDC MOF (microwave method)

In the PXRD of Cd –BDC MOF, synthesized by solvothermal method, the high intensity Bragg diffraction peaks are observed at $2\theta = 11.98, 15.06, 17.21, 24.26, 28.55,$ and 36.85° . The grain sizes are calculated as 3.81 nm and are found to be nano sized (Fig.10).

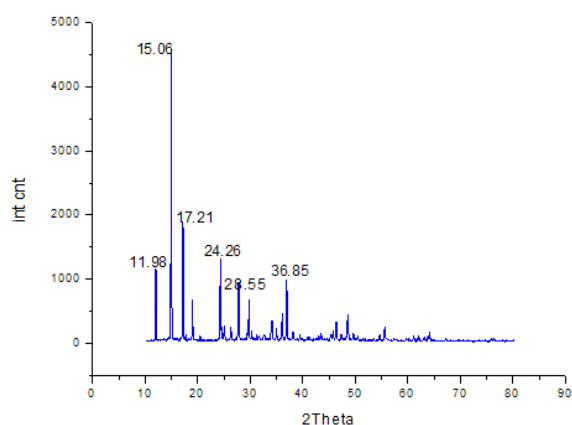


Fig.10. Powder XRD pattern of Cd-BDC MOF (solvothermal method)

In the PXRD of Cd –BDC MOF, synthesized by microwave method, the high intensity Bragg diffraction peaks are observed at $2\theta = 17.21, 17.81, 24.88, 27.03,$ and 32.24° . The average grain size is calculated as 5.1 nm and is found to be nano sized (Fig.11).

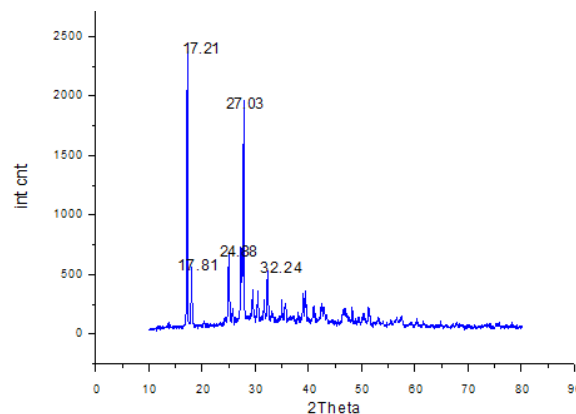


Fig.11. Powder XRD pattern of Cd-BDC MOF (microwave method)

In the PXRD of Ag –BDC MOF, synthesized by solvothermal method, the high intensity Bragg diffraction peaks are observed at $2\theta = 12.57, 16.45, 19.45, 28.08, 37.83, 31.05,$ and 44.21° . The average grain size is calculated as 3.56 nm and is found to be nano sized (Fig.12).

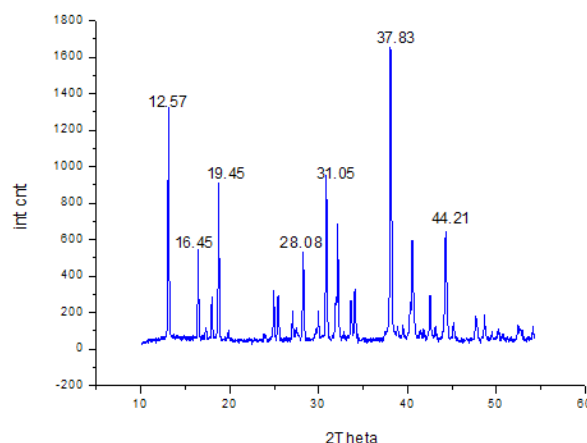


Fig.12. Powder XRD pattern of Ag-BDC MOF (solvothermal method)

In the PXRD of Ag–BDC MOF, synthesised by microwave method, the high intensity Bragg diffraction peaks are observed at $2\theta = 13.22, 17.21, 28.25, 31.68,$ and 41.14° . The average grain size is calculated as 5.1nm and is found to be nano sized (Fig.13). The 2θ values and the average grain sizes of all the MOFs have been summarized in Table 2. It is evident that method

of synthesis plays a role in the properties of MOFs.

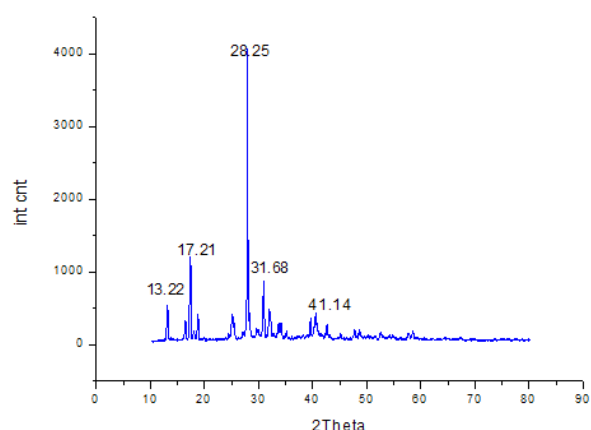


Fig.13. Powder XRD pattern of Ag-BDC MOF (microwave method)

SEM Analysis

The morphology of MOF crystals was studied by SEM. The SEM images of Zn-BDC MOF synthesized by different methods show different morphology (Figs. 14-16). The SEM image of Zn-BDC MOF synthesized by solvothermal method shows a flowery appearance for a single particle. The SEM of Zn-BDC MOF synthesized by microwave method shows irregular flake like pattern of MOFs.

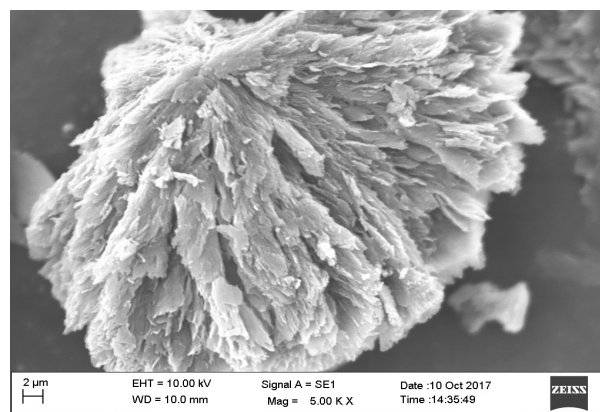


Fig.14. SEM image of Zn -BDC MOF single particle (solvothermal method)



Fig.15. SEM image of Zn -BDC MOF (solvothermal method)

The SEM image of Cd -BDC MOF synthesized by microwave method indicates the formation of nanorods. The SEM image of Cd -BDC synthesized by solvothermal method also indicates the formation of nanorods (Figs. 17-18).

Table 2. PXRD data of MOFs

MOF	High intensity Bragg diffraction peaks 2θ	Average grain size
Zn BDC MOF (Solvothermal)	13.52, 18.13, 22.42, 28.55 and 31.32°	3.81 nm
Zn BDC MOF (Microwave)	14.74, 16.29, 19.97, 22.12, 28.55 and 40.22°	4.78nm
Cd BDC MOF (Solvothermal)	11.98, 15.06, 17.21, 24.26, 28.55 and 36.85°	3.81nm
Cd BDC MOF (Microwave)	17.21, 17.81, 24.88, 27.03 and 32.24°	5.1nm
Ag BDC MOF (Solvothermal)	12.57, 16.45, 19.45, 28.08, 37.83, 31.05 and 44.21°	3.56nm
Ag BDC MOF (Microwave)	13.22, 17.21, 28.25, 31.68 and 41.14°	5.1nm

The SEM image of Ag –BDC synthesized by microwave method indicates the formation of crystalline particles arranged in an irregular fashion. The SEM image of Ag–BDC synthesised by solvothermal method also indicates the formation of crystalline particles arranged in an irregular fashion. The morphology is different for these MOFs synthesized by different routes (Figs. 19-20).

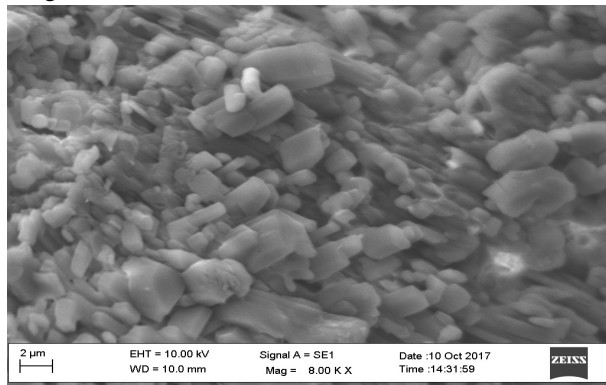


Fig.16. SEM image of Zn –BDC MOF (microwave method)

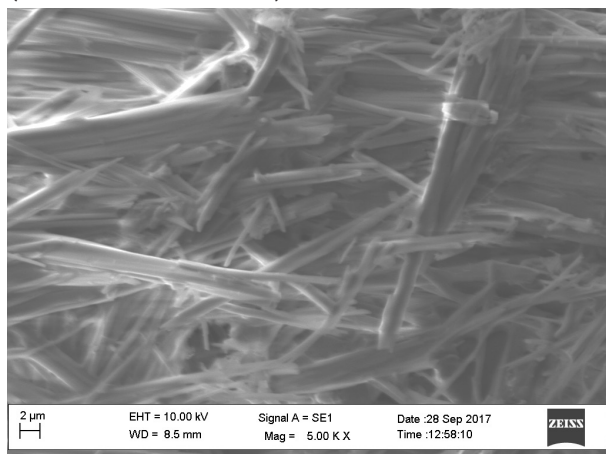


Fig.17. SEM image of Cd –BDC MOF (solvothermal method)

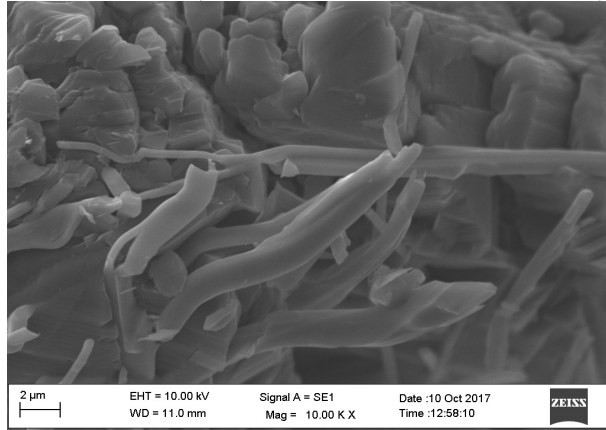


Fig.18. SEM image of Cd –BDC MOF (microwave method)

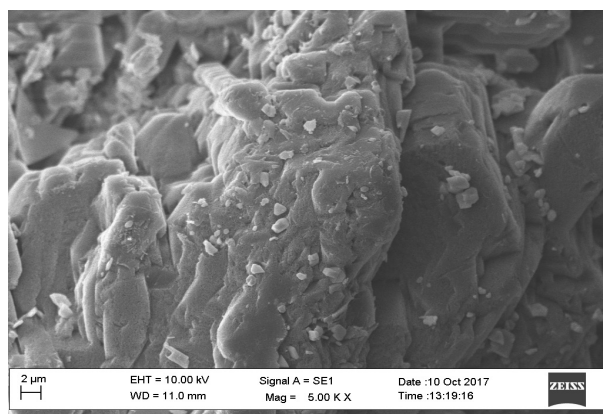


Fig.19. SEM image of Ag –BDC MOF (solvothermal method)

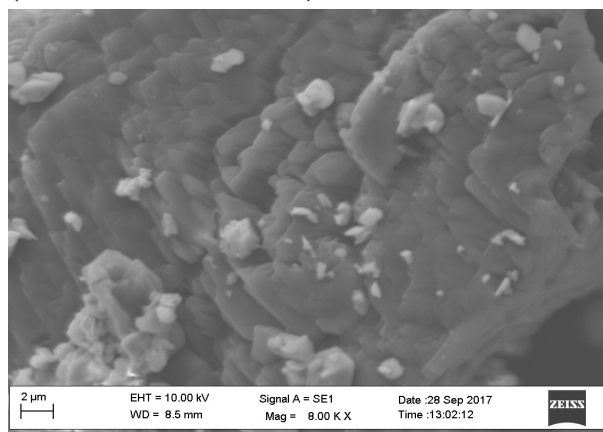


Fig.20. SEM image of Ag –BDC MOF (microwave method)

Energy Dispersive Spectroscopic Analysis (EDS)

The elemental analyses of metal organic frameworks of Cd and Ag with 1,4-Benzenedicarboxylic acid synthesized by solvothermal process were carried out using EDS analysis. The results are in agreement with the values of other transition MOFs (Pankaj K.Pal et al. 2014). The EDS spectra confirm the successful synthesis of all these MOFs.

Figures 21 & 22 represent the EDS of Cd-BDC MOF synthesized by two different methods: solvothermal and microwave processes. EDS show the presence of all the elements expected in the MOFs indicating the successful synthesis of MOFs. Different types of EDS are obtained for MOFs synthesized by different methods.

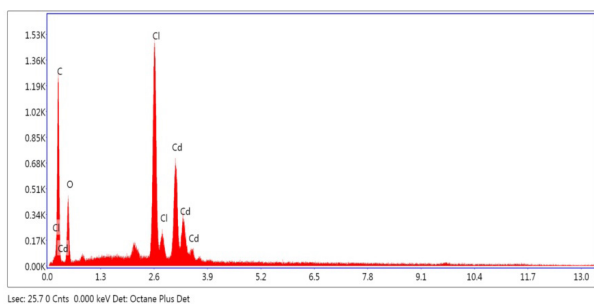


Fig.21. EDS of Cd-BDC MOF (solvothormal method)

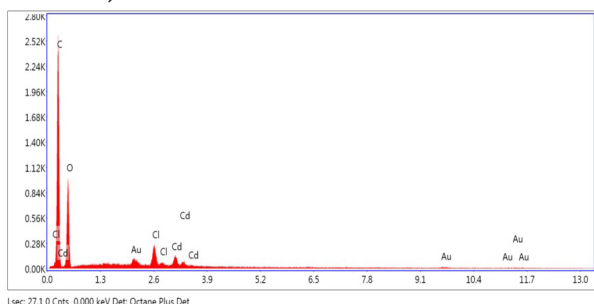


Fig.22. EDS of Cd-BDC MOF (microwave method)

Figures 23 & 24 represent the EDS of Ag-BDC MOF synthesized by two different methods. EDS show the presence of all the elements expected in the MOFs indicating the successful synthesis of MOFs. The spectra are different for MOFs synthesized by different methods.

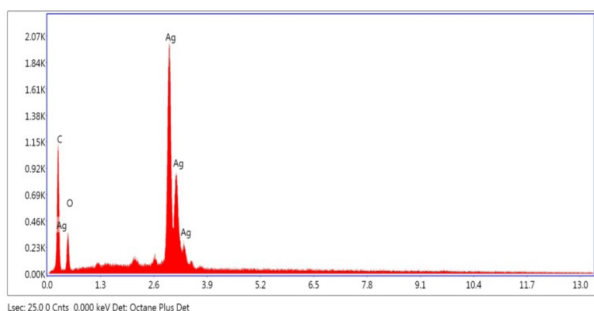


Fig.23. EDS of Ag-BDC MOF (solvothormal method)

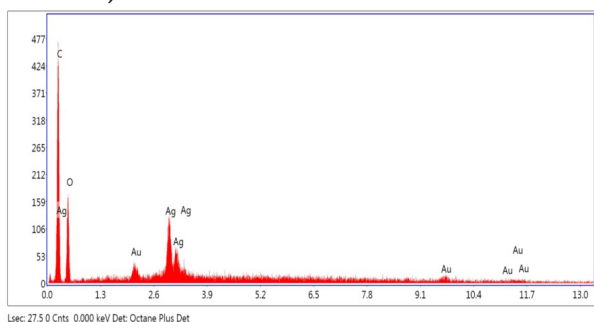


Fig.24. EDS of Ag-BDC MOF (microwave method)

Photoluminescence Studies

The solution state photoluminescence properties of the ligand and the synthesized MOFs have been investigated in methanol at room temperature from 400 -750nm. The ligand shows emission maxima at 331 when excited at 300nm, corresponding to $\pi-\pi^*$ and $n-\pi^*$ transitions and also due to the conjugation in the ligand (Fig. 25). The emission maxima are observed at 402nm, 427nm & 474nm in the case of Zn-BDC MOF synthesized by solvothormal method (Fig. 26); at 403nm, 426nm & 473nm in the case of Zn-BDC MOF synthesized by microwave (Fig. 27), when excited at 360nm; at 328nm in the case of Cd-BDC MOF synthesized by solvothormal method (Fig. 28); and at 329nm for Cd-BDC MOF synthesized by microwave method (Fig. 29) when excited at 300nm; at 456nm and 548nm for Ag-BDC MOF synthesized by solvothormal method (Fig.30) and at 403& 432nm for Ag-BDC MOF synthesized by microwave method (Fig.31), when excited at 360nm.

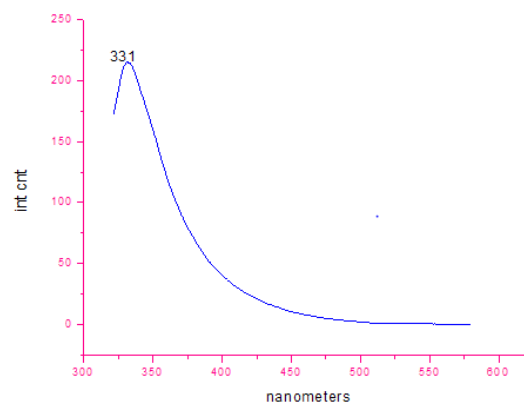


Fig.25. PL of BDC excited at 300nm

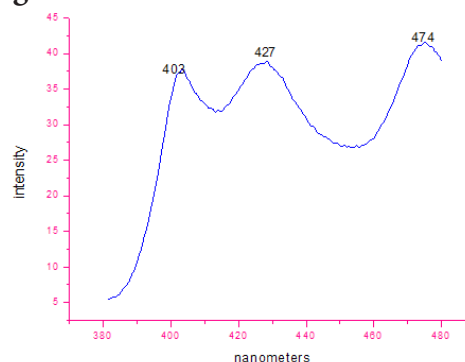


Fig.26. PL of Zn-BDC MOF (solvothormal) excited at 360nm

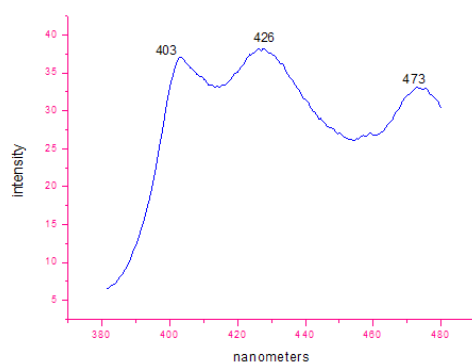


Fig.27. PL of Zn-BDC (microwave) excited at 360nm

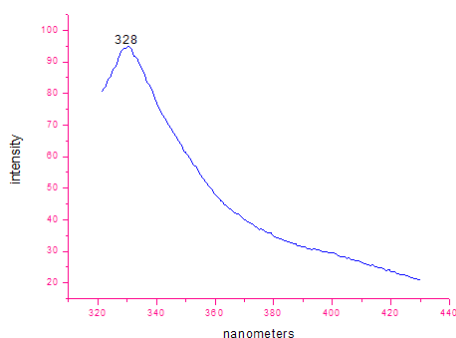


Fig.28. PL of Cd-BDC MOF (solvothermal) excited at 300nm

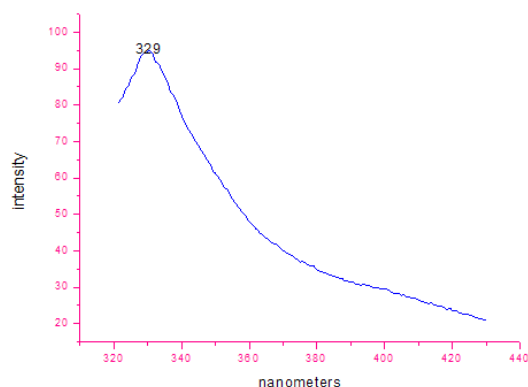


Fig.29. PL of Cd-BDC MOF (micro wave) excited at 300nm

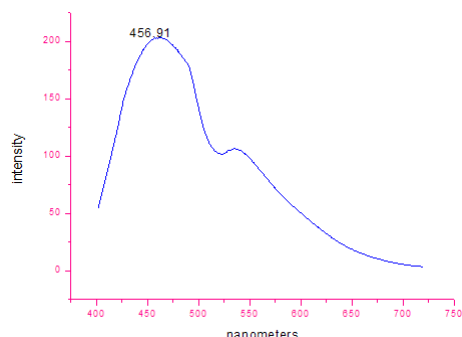


Fig.30. PL of Ag-BDC MOF (solvothermal) excited at 360nm

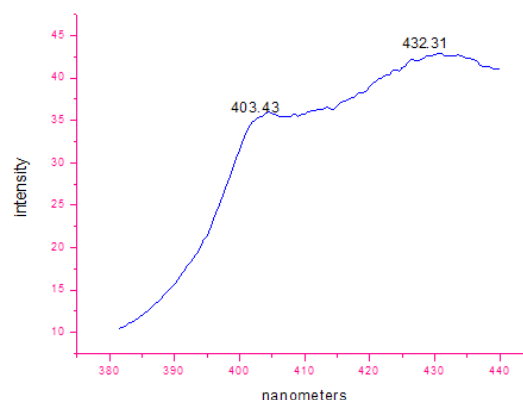


Fig.31. PL of Ag-BDC MOF (micro wave) excited at 360nm

The PL spectra indicate that the synthesized MOFs are luminescent in nature due to ligand centered emissions. The emission spectra of transition metal complexes are due to ligand centered emissions and charge transfer spectra. The metal ion does not seem to have an effect on the shape of the emission spectra. Detailed investigations on the luminescence lifetimes and quantum yields may provide the missing insights on the luminescence properties of these compounds. The photoluminescent spectra of various MOFs synthesized by different methods are also different. Single crystal X-ray diffraction studies may throw light into the reasons for the observed behavior.

SUMMARY

Nano crystalline and photo luminescent MOFs of 1,4- BDC using transition metal ions such as Zn(II), Cd(II) & Ag(II) have been synthesized successfully by hydrothermal approach and microwave synthesis. The MOFs synthesized using different methods have different morphologies and luminescent properties. These nano crystalline MOFs may find potential application as luminescent materials and in sensing applications. The method of synthesis plays an important role in the morphology, properties and hence the applicability of MOFs.

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Effect of lactone ring substituent in the Thermal Stability of Spiroborate Esters of Curcumin

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Abstract

The thermal stability of spiroborate esters of curcumin were largely depends on the substituent present in lactone ring. Structure activity relation studies will help to find the influence of these groups on determining the thermal stability. Thermal stability studies of rubrocurcumin were reported earlier. In the present work an analogue of rubrocurcumin was synthesized using lactic acid instead of oxalic acid. Thermal degradation studies were carried out using TG-DTG technique and its kinetic analysis was carried out. From the data obtained from thermogravimetric analysis various kinetic and thermodynamic parameters for thermal degradation were calculated using different non-isoconversional methods and the most suitable reaction model for thermal degradation was proposed. The activation energy obtained for this compound were compared with that reported for rubrocurcumin in order to find the effect of substituent in the lactone ring on the thermal stability.

Introduction

Curcumin is a natural polyphenolic compound found in the rhizomes of the plant turmeric commonly found in Asian countries [1]. The curcumin shows variety of remarkable biological properties like anti-carcinogenic[2], anti-inflammatory[3], anti-oxidant activity [4]etc. Besides curcumin its analogues and metal complexes also shows remarkable pharmacological activities[5-8]. Among curcumin metal complexes, its boron complexes commonly called as spiroborate esters of curcumin are less studied due to its difficulty in preparing the compound in its pure form because of its less hydrolytic stability[9-10].

Rubrocurcumin and rosocyanin are the two well-known spiroborate esters of curcumin. The less hydrolytic stability of these compounds in water mediated condition limits its application as the spectrophotometric reagent in boron determination[11]. The hydrolyzing property of these compounds in water mediated conditions

makes them a good carrier of curcumin in biological systems. The thermal and hydrolytic stability studies of rubrocurcumin and rosocyanin are reported earlier[12-13]. It will be interesting to study the influence of lactone ring in the stability spiroborate esters of curcumin by altering structural features of the ring.

In the present work an analogue of rubrocurcumin was synthesized by replacing the dicarboxylic acid; oxalic acid with a hydroxy acid; lactic acid. The spiroborate ester of curcumin with lactic acid (CBL) differs from rubrocurcumin in one C=O group (Figure 1). The C=O group in rubrocurcumin is replaced by CH-CH₃ group in CBL. The IR and ¹H NMR spectra obtained corresponds to that reported in literature [14]. Along with UV-Visible and IR, ¹H NMR, ¹³C and ¹¹B NMR spectra confirm the proposed structure of CBL. Non-isothermal thermogravimetric method has been used to study thermal degradation of CBL. Both

differential and integral method were used to study the kinetics of thermal degradation. The main objective of the present study is to compare the thermal stability of CBL with rubrocurcumin in order to find the influence of lactone C=O group in the thermal stability of spiroborate esters of curcumin.

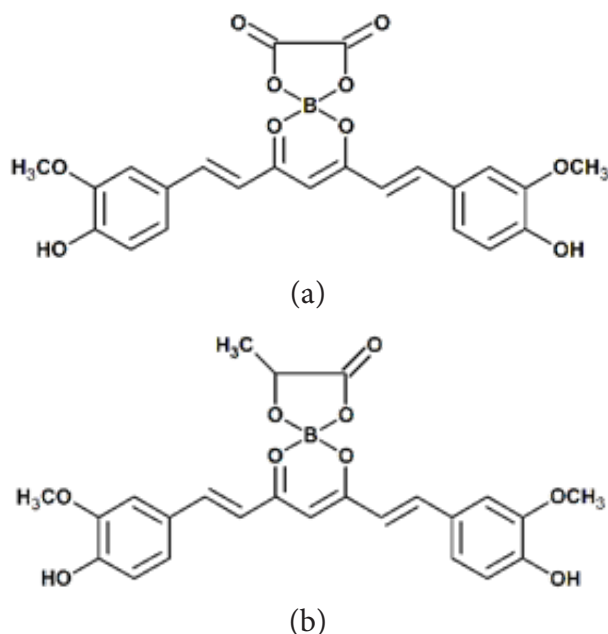


Figure 1. Structure of rubrocurcumin (a) and CBL (b).

Materials and methods

The curcumin used for the preparation of CBL were column chromatographically purified from commercial curcumin using column chromatography[15]. Boric acid and lactic acid purchased from Merk Chemie Pvt. Ltd., India were used as received without any further purification. CBL were subjected to thermogravimetric analysis studies at a rate of 10 °C/min in nitrogen atmosphere using Perkin-Elmer Thermogravimetric Analyzer.

Synthesis of CBL

A solution of curcumin (1mmol), boric acid (1mmol) and lactic acid (1mmol) in toluene was heated at 90 °C for 3-4 hours with stirring (Figure 2). The completion of reaction was tested by TLC through the disappearance of spot for curcumin. The precipitated CBL was collected by filtration. The crude yield of CBL after washing with toluene and reprecipitated from ethyl acetate was 78%[14]. UV λ_{max} =

509 nm, $\epsilon = 4.75 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (acetone); IR (KBr, cm^{-1}): 3445 (brd, OH), 1729 (shp, C=O in lactone ring), 1515 (shp, C=O in curcumin), 1153 (shp, C-O in phenol), 1080 (m, C-O in OCH_3); ^1H NMR (400 MHz, DMSO-d_6): δ 1.37 (d, $J = 6.8 \text{ Hz}$, 3H, CH_3), 3.86 (s, 6H, OCH_3), 4.43-4.48 (m, 1H, CH), 6.51 (s, 1H, CH), 7.34 (d, $J = 14.8 \text{ Hz}$, 2H, Ar-H), 6.87 (d, $J = 9.2 \text{ Hz}$, 2H, Ar-H), 7.47 (s, 2H, Ar-H), 7.92 (d, $J = 19.2 \text{ Hz}$, 2H, =CH), 7.01 (d, $J = 15.6 \text{ Hz}$, 2H, =CH), 10.10 (s, 2H, OH); ^{13}C NMR: 20.41, 55.74, 71.50, 100.78, 112.45, 115.93, 117.88, 125.17, 125.97, 146.94, 148.15, 151.33, 178.61, 183.17.

Thermal analysis

CBL (~ 3 mg) taken in alumina crucible were heated from 40 to 700 °C under nitrogen atmosphere (flow rate of 100 cm^3/min). Empty alumina crucible was the reference. The nonisothermal TGA runs were conducted at a heating rate 10 °C/min. The non-isoconversional model fitting methods were used for kinetic analysis. Different non-isoconversional methods used in this study includes that of Coats Redfern (CR)[16], Broido (BR) [17], Madhusudanan Krishnan Ninan (MKN) [18], Sharp Wentworth (SW) [19], Freeman Carrol(FC)[20], Achar (AC) [21] and Horowitz Metzger [22].

Results and discussion

Thermal decomposition thermogram of CBL at a heating rate 10°C min⁻¹ is presented in Figure 2. The thermogram of CBL shows two stages of degradation. The initial decomposition was observed within the temperature range 40 to 150 °C with a weight loss of 1.44% and is due to the removal of hydrogen bonded water molecule. The second stage shows a weight loss of 15.34/15.38 % (calcd. /found) within the temperature range 234 to 295 °C may attribute to the loss of lactate group. A continuous weight loss was then observed beyond 295 °C due to the degradation of curcumin. The final product in the thermal degradation is boric oxide and the mechanism for thermal degradation is given in figure 3. The same degradation pattern is observed for the rubrocurcumin in which oxalic acid is coordinated to boron [12].

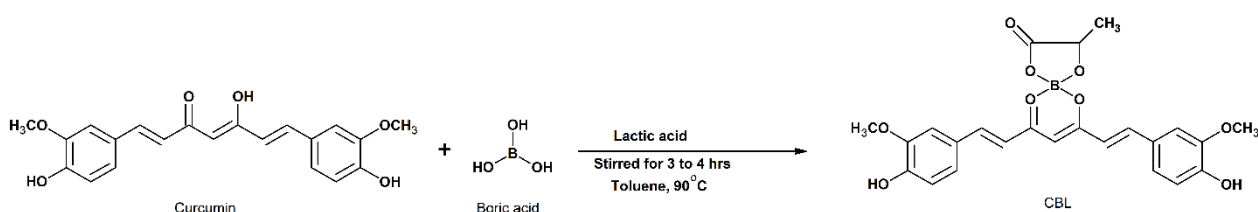


Figure 2. Scheme for the synthesis of CBL.

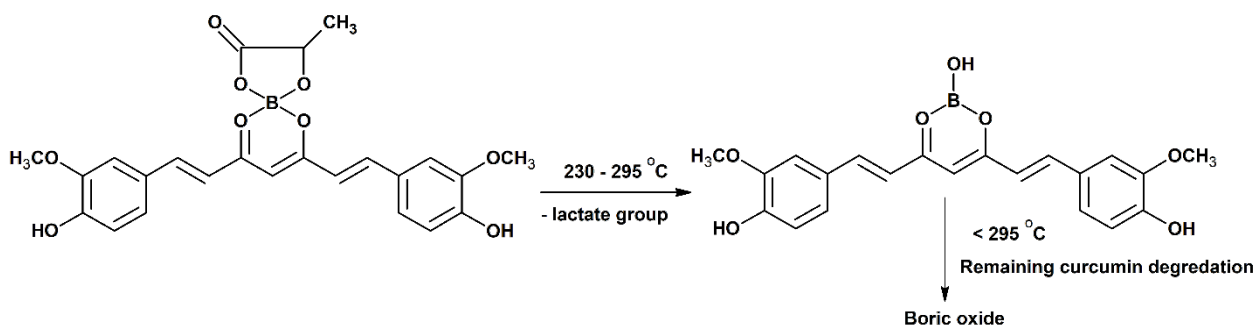


Figure 3. Thermal degradation mechanism of CBL.

Table 1. Correlation coefficients obtained for different solid state reaction models.

Reaction model	$g(\alpha)$	Correlation coefficient (R^2)
First order	$[-\ln(1-\alpha)]$	0.9975
Zero order	α	0.9797
Second order	$[(1-\alpha)^{-1}-1]$	0.9797
Avrami-Erofe'ev(A2)	$[-\ln(1-\alpha)]^{1/2}$	0.9932
Avrami-Erofe'ev(A4)	$[-\ln(1-\alpha)]^{1/4}$	0.9925
Power law (P2)	$\alpha^{1/2}$	0.9783
One dimensional diffusion(D1)	α^2	0.9804
Two dimensional diffusion(D2)	$[(1-\alpha)\ln(1-\alpha)]+\alpha$	0.9914
Three dimensional diffusion(D3)	$[1-(1-\alpha)^{1/3}]^2$	0.9023
Contracting area(R2)	$[1-(1-\alpha)^{1/2}]$	0.9113
Contracting volume(R3)	$[1-(1-\alpha)^{1/3}]$	0.8655

Table 2. Thermal and kinetic parameters of CBL obtained from different non-isoconversional methods

Method	R^2	E_a (kJ mol ⁻¹)	A (s ⁻¹)	$\Delta H^\#$ (kJ mol ⁻¹)	$\Delta S^\#$ (J mol ⁻¹ K ⁻¹)	$\Delta G^\#$ (kJ mol ⁻¹)
CR	0.9935	350.64	3.59×10^{32}	346.21	364.99	151.30
BR	0.9938	359.57	2.65×10^{33}	355.13	381.77	151.26
MKN	0.9936	350.82	2.22×10^{33}	346.38	380.33	143.29
HM	0.9953	369.69	3.79×10^{34}	365.25	403.90	149.57
SW	0.9369	383.19	5.42×10^{36}	378.47	444.64	125.46
AC	0.9995	373.32	3.25×10^{37}	376.41	459.54	116.99
FC	0.9995	344.69	3.25×10^{37}	344.67	459.54	116.99

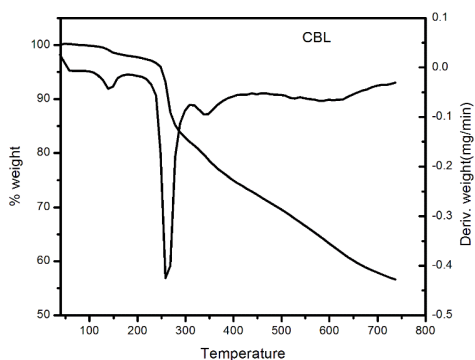


Figure 2. TG-DTG curve for the thermal degradation of CBL.

Kinetic analysis

Determination of solid state reaction model

Eleven solid state reaction models reported in literature [23] were used to find out the best kinetic model that represents the thermal decomposition of CBL. CR method were used for this purpose. Each reaction model has their unique $g(\alpha)$ expression which determines the solid state reaction mechanism through which it degrades. This function $g(\alpha)$ corresponding to different reaction models are substituted in LHS of CR equation and the corresponding plots are drawn for each reaction models using $\ln(g(\alpha)/T^2)$ vs $1/T$. Out of the eleven different solid state reaction models which give better correlation coefficient (R^2) nearer to one is the probable thermal decomposition mechanism of the complex [23]. The R^2 value calculated for the compound for different solid state reaction models are given in Table 1. The first order reaction model commonly called as Mampel power law fits to the degradation processes of CBL.

Determination of kinetic parameters

The decomposition of CBL starts when the lactic acid ring degrades. The kinetic parameters associated with the thermal decomposition of this stage, evaluated using CR, BR, MKN, SW, AC, HM and FC methods are given in Table 2. Corresponding computerized plots are given in Figure 4. Considering the differences in the values of the kinetic parameters calculated using different methods, it can be concluded that the differences observed due to different calculation methods are relatively small and are comparable.

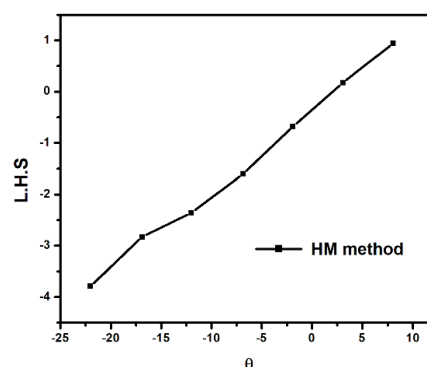
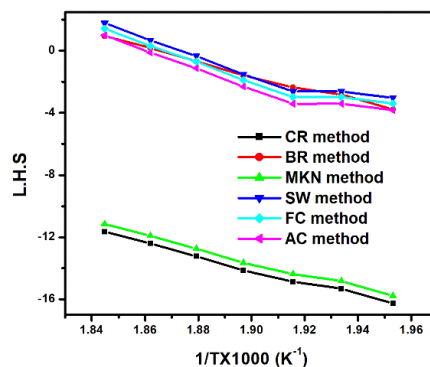


Figure 4. Different non-isoconversional plots for the thermal degradation of CBL.

The linearity in these plots indicates the order of thermal decomposition as unity [23]. The activation energy (E_a) of the complex increases with increase in their thermal stability. The positive value for activation energy indicates that there is no phase transition during the thermal decomposition [24]. High activation energy ($E_a > 10 \text{ kJmol}^{-1}$) of CBL revealed their high thermal stability [25]. The positive value of $\Delta H^\ddagger$ indicates the endothermic nature of thermal decomposition [25]. The value of $\Delta S^\ddagger$ is positive which indicate the irreversible nature of degradation. Non-spontaneity of thermal decomposition is shown by the positive value of $\Delta G^\ddagger$ [25].

Effect of C=O group in the thermal stability of spiroborate esters of curcumin

The rubrocurcumin and CBL differ by a C=O group in lactone ring; one of the $-\text{C}=\text{O}$ group of rubrocurcumin is replaced by $-\text{CH}-\text{CH}_3$ group in CBL. A detailed study on the thermal degradation of rubrocurcumin was reported by the present group [12, 26], the reported E_a values were presented along with that of CBL in table 3.

Compound	<i>Ea</i> (kJ mol ⁻¹) obtained from different non-isoconversional methods						
	CR	BR	MKN	AC	SW	FC	HM
CBL	350.64	359.57	350.82	373.32	383.19	344.69	369.69
Rubrocurcumin	683.19	630.62	620.89	653.05	653.05	615.92	687.99

Table 3. Comparison table for *Ea* value for rubrocurcumin and CBL.

The activation energy value were greater for rubrocurcumin which indicates the higher stability of rubrocurcumin over CBL. The replacement of one C=O group of rubrocurcumin by -CH-CH₃ group in CBL, changes one ester bonds to ether bond with boron. Since the ether bonds are labile than ester bonds the stability of CBL is less than rubrocurcumin.

Conclusion

Curcumin and its analogues are known for its pharmacological activities. Less bioavailability of curcumin is the main problem encountered in using them as a therapeutic drug. Curcumin boron complexes are used in analytical application for determining boron presence in various matrices. These complexes are hydrolytically less stable and hence suitable for the carriers of curcumin. The stability studies are important and the structural activity relationship is essential in view of their application as drug candidates. The present study reveals that CBL, the spiroborate ester of curcumin with lactic acid is less stable than rubrocurcumin, the spiroborate ester of curcumin with oxalic acid.

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Biosynthesis of Silver Nanoparticles and Evaluation of its Anti-Bacterial Property

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ABSTRACT

The present work reports a simple, cost – effective, and ecofriendly method for the synthesis of silver nanoparticles (AgNPs) using *coleus aromaticus* leaves extracts. The formation of AgNPs was confirmed by colour change, AgNPs appears brown colour in aqueous medium due to surface plasmon vibration. The synthesized silver nanoparticles were further characterized by ultraviolet- visible absorption spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), Dynamic light scattering (DLS), Zeta potential, Transmission Electron microscopy(TEM) and X-ray diffraction spectroscopy (XRD). The ultraviolet- visible spectroscopy results show peak in between 430-450nm which is the characteristic peak of AgNPs. FTIR study demonstrates flower and leaf extracts acted as the reducing and stabilizing agent during the synthesis. The DLS studies reveals that the silver nanoparticles are having spherical shapes and the average size ranged between 67-104nm. The zetapotential values shows that the synthesized silver nanoparticles are having incipient instability. The TEM images shows the size distribution of the nanoparticles and the particle size was found to be 10-30nm. XRD result shows that size of the nanoparticles is 26.6nm. XRD study corroborated exactly with that of TEM. Antibacterial activity of the synthesized silver nanoparticles was tested with gram negative organisms such as *Escherichia coli*, *pseudomonas aeruginosa*, *salmonella typhi* and gram positive organisms such as *Bacillus subtilis* and synthesised silver nanoparticles have considerable effect on *Escherichia coli* and *Bacillus subtilis*.

Keywords: *Coleus Aromaticus* leaves, Silver nanoparticles, UV-Vis, FTIR, DLS, Zeta potential, TEM, XRD, Antibacterial activity.

INTRODUCTION

One of the most active areas of research of modern era is the nanotechnology. Nanoparticles are particles having size in between 1-100nm and which shows a wide variety of properties in contrast to its larger particles in bulk material. Due to the unique properties of metal nanoparticles which includes catalytic activity, optical property, electronic property, magnetic property etc. they are widely studied. Usually metal nanoparticles are synthesized via chemical route [1-4]. Nowadays, the green synthesis of nanoparticles

has attained greater importance than chemical method because the greener alternatives are environmental friendly, cheap and low cost[5]. Among the metal nanoparticles, silver has been extensively studied because of its unique physical, chemical and biological properties. In the conventional method of synthesizing silver nanoparticles, toxic substances such as borohydrides, hydrazines etc. are used as reducing agents. In the green technique, the extracts from various parts of a plant such as leaves, flowers, fruits etc. were used as the

reducing and capping agents [6-10]. Silver nanoparticles have wide applications in the field of medicine because of its high antibacterial property [11-15]. The present work reports the green synthesis of silver nanoparticles from *Coleus aromaticus* leaves extract and evaluation of its antibacterial property.

MATERIALS

Analytical grade AgNO_3 was obtained from Sigma – Aldrich chemicals and used as received. *Coleus aromaticus* leaves were collected from local areas in Alappuzha district in Kerala, India. Distilled water was used to perform the experiments.

Four pathogenic bacterial strains procured from microbial type culture collection (MTCC, Chandigarh, India) were employed in the present study to investigate the antibacterial properties of the synthesized AgNPs. *Staphylococcus*, *Salmonella typhi*, *E. coli*, *Pseudomonas* were used as the test pathogens for the antibacterial study.

METHODS

Preparation of the leaf extract and 1mM AgNO_3

Fresh and healthy leaves were collected locally and rinsed thoroughly first with tap water followed by distilled water to remove all the dust and unwanted visible particles, cut into small pieces and dried at room temperature. About 10g of these finely incised leaves were weighed and transferred into 250ml beaker containing 100ml distilled water and boiled for about 20 min. The extract was filtered thrice through Whatman No.1 filter paper to remove particulate matter and to get clear solution. 0.084g silver nitrate was added to 500ml of distilled water and dissolved thoroughly.

Biosynthesis of silver nanoparticles (AgNPs)

Take 2.5ml, 5 ml and 7.5ml of leaf extract in different beakers. Then, 100 mL of AgNO_3 (1 mM) aqueous solution was reacted with leaf extract solutions at room temperature. The reaction mixture was kept undisturbed until the colourless solution converted into a reddish-brown colour, which indicated the formation of AgNPs. The particles were then purified by centrifugation at 5000rpm for 10 minute. It was used for further studies.

CHARACTERIZATION OF SILVER NANOPARTICLES:

UV-Vis Analysis

The reduction of silver ions was monitored by measuring the UV-Vis spectrum of the reaction mixture by using a UV-Vis spectrophotometer (Shimadzu model) in the wavelength ranging from 300–650 nm.

FTIR analysis

The chemical composition of the synthesized silver nanoparticles was studied by using FTIR spectrometer (Perkin-Elmer LS-55-Luminescence spectrometer). For removing the biochemical compound or uncapping ligands of nanoparticle, the 500ml solution of silver nanoparticles was centrifuged at 5000rpm for 10 minute and suspension was taken. Then FTIR analysis of silver nanoparticles was carried out through the potassium bromide (KBr) pellet (FTIR grade) method.

DLS & Zeta-Potential Analysis:

Dynamic light scattering (DLS) which is based on the laser diffraction method with multiple scattering techniques was employed to study the average particle size of silver nanoparticles. The prepared sample was dispersed in deionised water followed by ultra-sonication. Then solution was filtered and centrifuged for 15 min. at 25° C with 5000 rpm and the supernatant was collected. The supernatant was diluted for 4 to 5 times and then the particle distribution in liquid was studied in a computer controlled particle size analyser (ZETA seizer Nano series, Malvern instrument Nano Zs).

Transmission Electron Microscopy (TEM)

TEM shows the shape and the crystal structure (if any) as well as size of the particles. The grid for TEM analysis was prepared by placing a drop of nanoparticles suspension on a carbon coated copper grid and alloying the water to evaporate inside a vacuum drier. The grid containing silver nano particles was scanned by Transmission Electron Microscope

XRD Analysis

The phase variety and grain size of synthesized Silver nanoparticles was determined by X-ray diffraction spectroscopy

(Philips PAN analytical). The synthesized silver nanoparticles were studied with radiation at voltage of 30 kV and current of 20 mA with scan rate of 0.03°/s. Different phases present in the synthesized samples were determined by X'pert high score software with search and match facility. The particle size of the prepared samples were determined by using Scherer's equation as follows

$$D \approx 0.9\lambda / \beta \cos\theta$$

Where D is the crystal size, λ is the wavelength of X-ray, θ is the Bragg's angle in radians and B is the full width at half maximum of the peak in radians.

Anti-bacterial studies

Four bacterial strains were employed in the study to investigate the antibacterial properties of the plants. The gram negative organisms such as *Escherichia coli* MTCC 585, *Pseudomonas*, *Salmonella typhi* and gram positive organisms such as *Staphylococcus* were used to study the antibacterial property of green synthesised silver nanoparticles under investigation. Bacterial strains were streaked on nutrient agar and the single pure culture were streaked on nutrient agar slants and stored at 4°C to keep the strains viable. Nutrient agar (for the test and storage) and nutrient growth (for sub culturing) were used

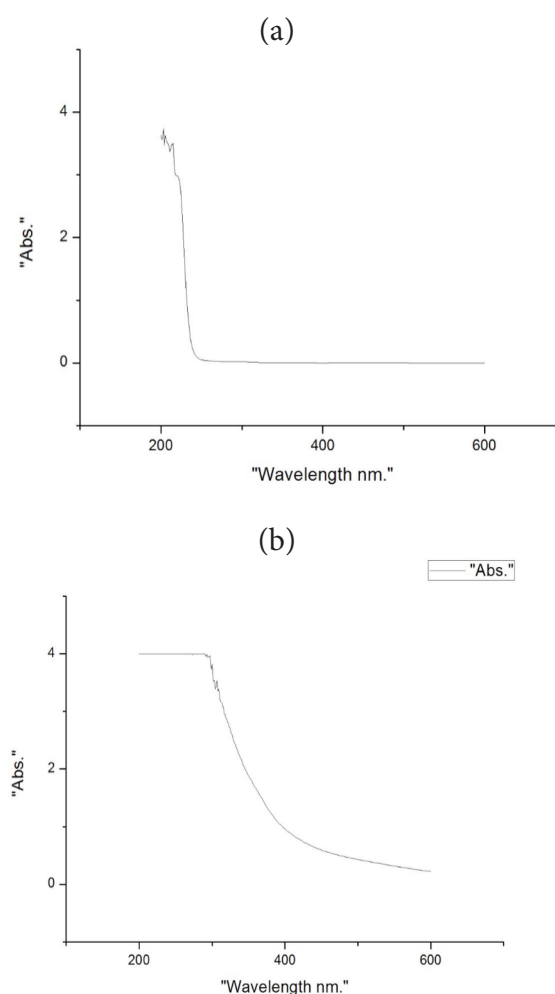
RESULTS & DISCUSSION

In the present study, AgNPs were synthesized from the leaf extracts of *Coleus aromaticus*. Flavonoids, tannins, proteins, and reducing sugars that are present in plants may be responsible for the formation of AgNPs by reducing AgNO_3 . These constituents can act as bioreductants and capping agents. It was observed that the reduction of silver ions into AgNPs was confirmed by the change of the silver nitrate solution to a reddish-brown color within 5 minutes at room temperature whereas the control AgNO_3 solution (without the leaf extract) showed no change in color. This characteristic difference in color is due to the excitation of the surface plasmon resonance in the metal NPs. The formation of AgNPs was further confirmed by using ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR), transmission

electron microscopy (TEM), DLS, zeta potential X-ray diffraction spectroscopy (XRD) and antibacterial study.

UV-VIS ANALYSIS

Silver nanoparticles appear brown in colour in aqueous medium as a result of surface plasmon vibration. The metal nanoparticles have free electrons, which give the SPR absorption band, due to the combined vibration of electrons of metal nanoparticles in resonance with light wave. As the leaf extract was added to aqueous silver nitrate solution, the colour of the solution changed from faint yellow to reddish yellow to reddish brown and finally to colloidal brown indicating AgNPs formation. **Figure 1** shows the UV-vis absorption spectrum of the AgNO_3 leaf extract and synthesized AgNPs. A broad absorption peak was observed at 430-450 nm, which is a characteristic band for the Ag, arising from the excitation of longitudinal plasmon vibrations of AgNP in the solution.



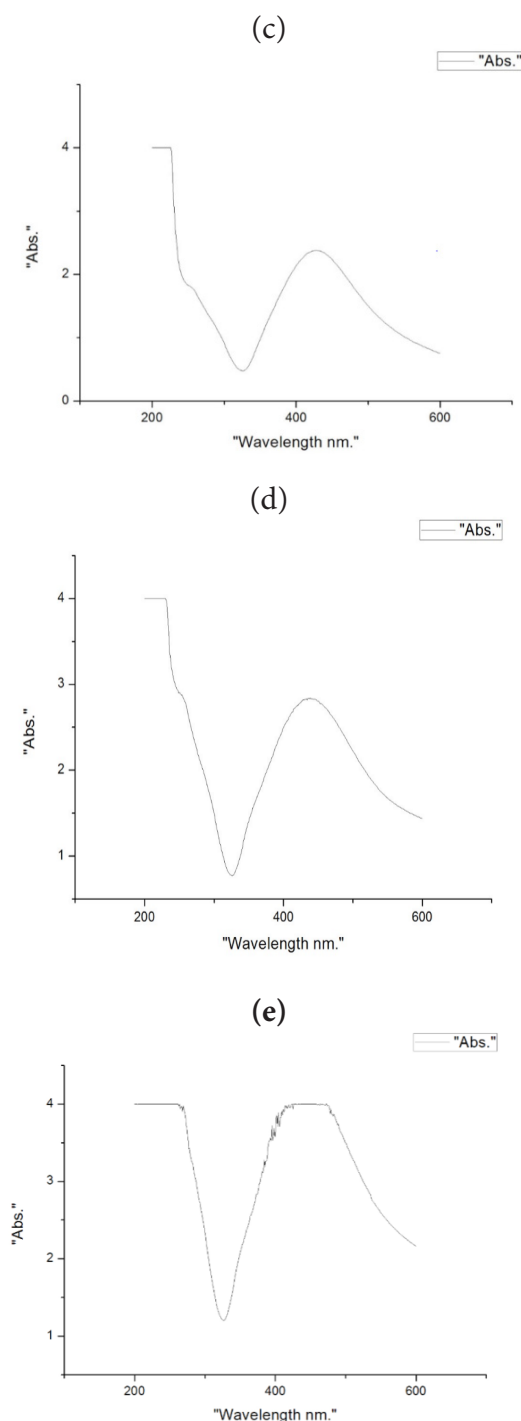


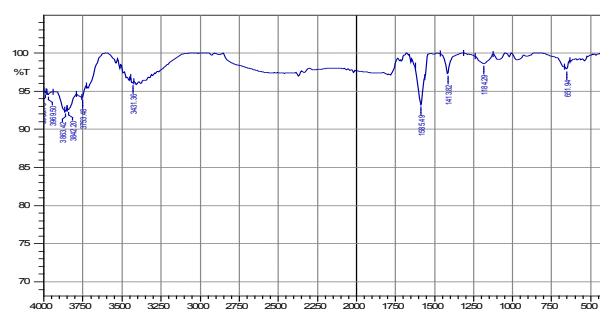
Figure 1: UV-visible spectra of (a) silver nitrate solution (AgNO_3) (b) *coleus aromaticus* leaf extract (c) (2.5 ml leaf extract + 1 mM AgNO_3) (d) (5 ml leaf extract + 1 mM AgNO_3) (e) 7.5ml leaf extract+1mM AgNO_3

FTIR ANALYSIS

FTIR measurements were carried out to identify the biomolecules for capping and efficient stabilization of the metal nanoparticles synthesized. The FTIR spectrum of silver nanoparticles in figure showed that the band between $3490\text{--}3500\text{ cm}^{-1}$ corresponds to O-H

stretching H-bonded alcohols and phenols. The peak found around $3400\text{--}3250\text{ cm}^{-1}$ showed a stretch for N-H bond, peak around $1500\text{--}1400\text{ cm}^{-1}$ showed the bond stretch for C-C bond. Peak around $1500\text{--}1475\text{ cm}^{-1}$ showed N-O asymmetric stretching whereas the stretch for AgNPs were found around $500\text{--}550\text{ cm}^{-1}$. Therefore the synthesized nanoparticles were surrounded by proteins and metabolites such as terpenoids having the above mentioned functional groups. From the analysis of FTIR studies we confirmed that the carbonyl groups from the amino acid residues and proteins has the stronger ability to bind metal indicating that the proteins could possibly from the metal nanoparticles (i.e.; capping of silver nanoparticles) to prevent agglomeration and thereby stabilize the medium. This suggests that the biological molecules could possibly perform dual functions of formation and stabilization of silver nanoparticles in the aqueous medium. Carbonyl groups proved that flavanones or terpenoids were absorbed on the surface of metal nanoparticles. Flavanones or terpenoids could be adsorbed on the surface of metal nanoparticles, possibly by interaction through carbonyl groups or *p*-electrons in the absence of other strong ligating agents in sufficient concentration. The presence of reducing sugars in the solution could be responsible for the reduction of metal ions and formation of the corresponding metal nanoparticles. It is also possible that the terpenoids play a role in reduction of metal ions by oxidation of aldehydic groups in the molecules to carboxylic acids. These issues can be addressed once the various fractions of the *coleus aromaticus* leaf extract are separated, identified and individually assayed for reduction of the metal ions.

(a) Silver nitrate



DYNAMIC LIGHT SCATTERING

The analysis of correlogram obtained from dynamic light scattering measurement, that is light (zenon, Deuterium) is passed through sample1 (take 200 μ l from 2.5ml sample then add 3ml distilled water into it) and analyse reflected light, then calculate the size and shape of the particle. Follow same procedure for 5ml and 7.5ml samples. The graph (figure: a, b, & c) shows that it may contain silver nano particle which is spherical in shape. According to size distribution report by intensity graph (figure A), it is evident that silver nanoparticle having size in between 10-100 nm with average mean size of 67.45nm .(In figure B) silver nanoparticle having size in between 10-100 nm with mean average size of 87.22nm .(In figure C) it is also evident that silver nanoparticle having size in between 10-1000nm with average size range from 104.4nm is present. These are also supported by size number graph (figure D, E,F).

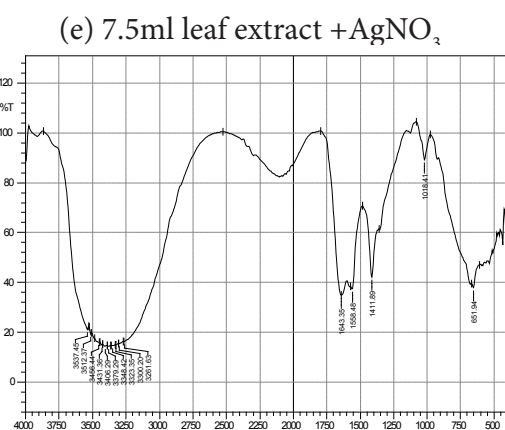
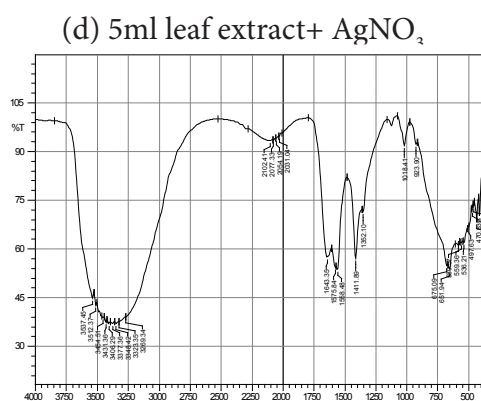
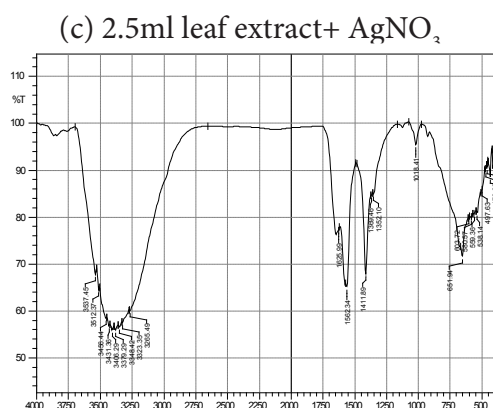
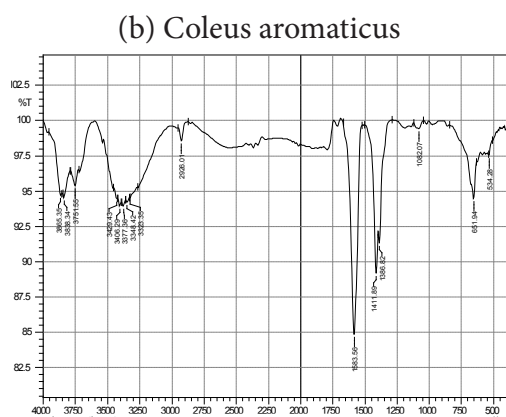
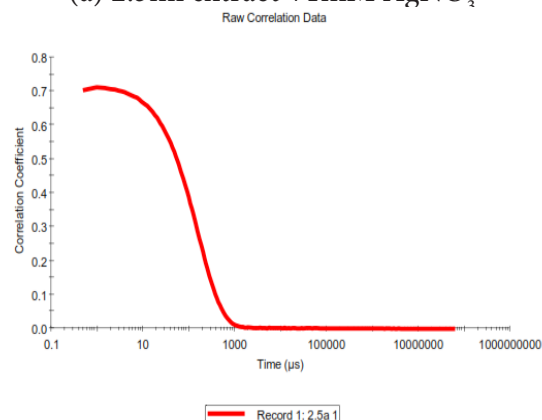
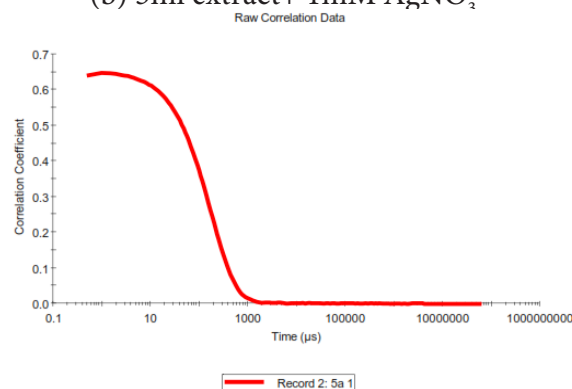


Figure 2: FTIR analysis of (a) silver nitrate solution (AgNO_3) (b) *coleus aromaticus* leaf extract (c) AgNPs (2.5 ml leaf extract + 1 mM AgNO_3) (d) (5 ml leaf extract + 1 mM AgNO_3) (e) 7.5ml leaf extract+1mM AgNO_3

(a) 2.5ml extract + 1mM AgNO_3



(b) 5ml extract+ 1mM AgNO_3



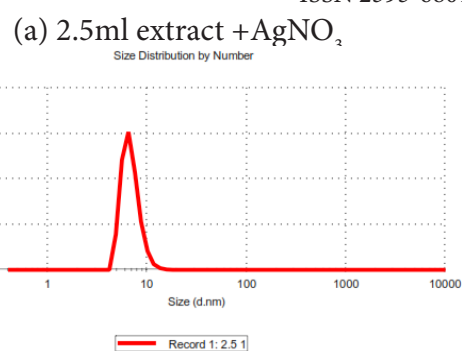
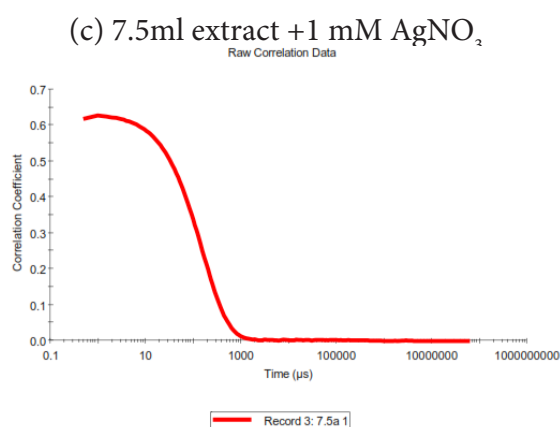


Figure 3: correlogram of (a) 2.5ml extract + AgNO_3 (b) 5ml extract + AgNO_3 (c) 7.5ml extract + AgNO_3

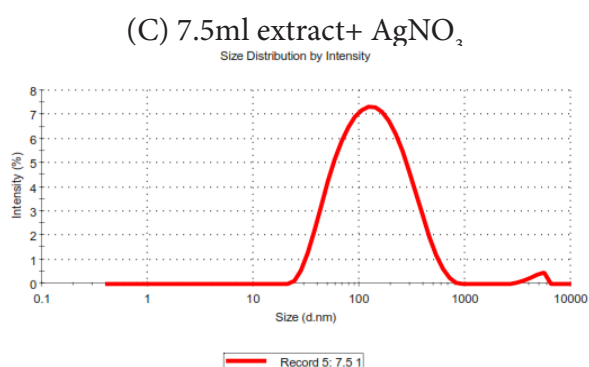
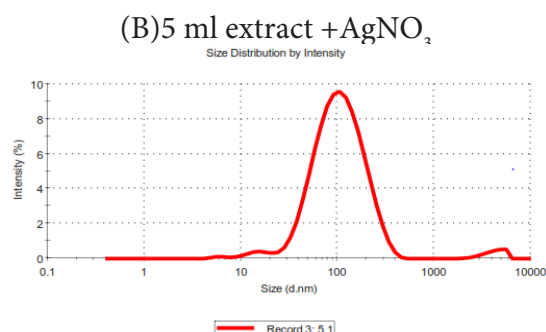
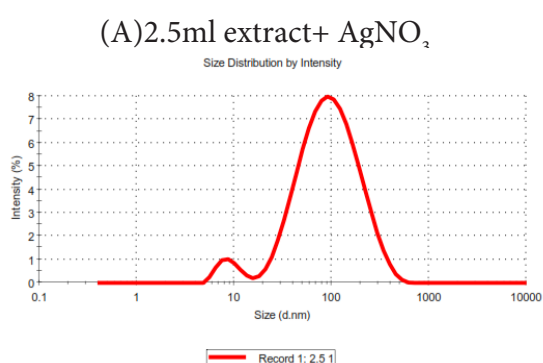


Fig 4: DLS showing size distribution by intensity graph of (A) 2.5ml extract + 1Mm AgNO_3 (B) 5ml extract + 1mM AgNO_3 (C) 7.5ml extract + 1Mm AgNO_3

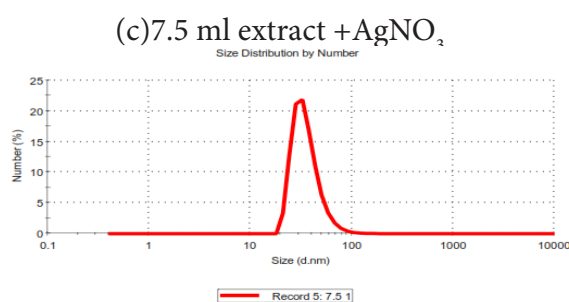
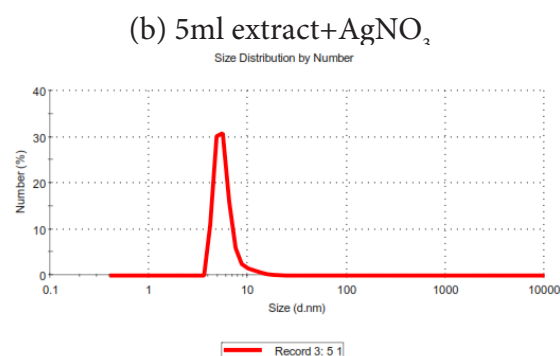


Fig 5: size distribution by number graph of (a) 2.5ml extract + 1Mm AgNO_3 (b) 5ml extract + 1mM AgNO_3 (c) 7.5 extract + 1Mm AgNO_3

ZETA POTENTIAL

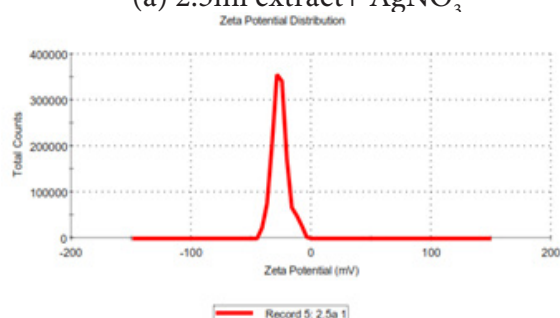
The zeta potential is a key indicator of the stability of nanoparticles. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. Those nanoparticles having high zeta potential value (negative or positive) denotes they are electrically stabilized. Here the zeta potential measurements of silver nanoparticles synthesized with different proportions like 2.5ml extract + AgNO_3 (figure a), 5ml extract + AgNO_3 (figure b), 7.5ml extract + AgNO_3 (figure c). From the analysis the order of stability of nanoparticles synthesized from different

The zeta potential has direct relationship with the stability of a form structure as shown in table (1) given below.

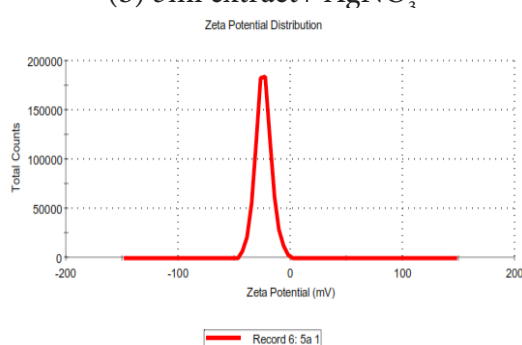
Zeta potential [mV]	Stability behavior of the colloid
from 0 to ± 5	Rapid coagulation or flocculation
from ± 10 to ± 30	Incipient instability
from ± 30 to ± 40	Moderate stability
from ± 40 to ± 60	Good stability
more than ± 61	Excellent stability

proportions are 2.5ml extract + AgNO₃ > 5ml extract + AgNO₃ > 7.5ml extract + AgNO₃. The values of zeta potentials are -25.8mV, -23.8mV, -18.6mV respectively. So the stability of these nanoparticles explained in terms of incipient instability.

(a) 2.5ml extract+ AgNO₃



(b) 5ml extract+ AgNO₃



(c) 7.5ml extract+ AgNO₃

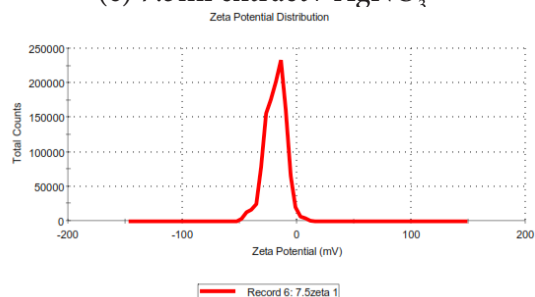
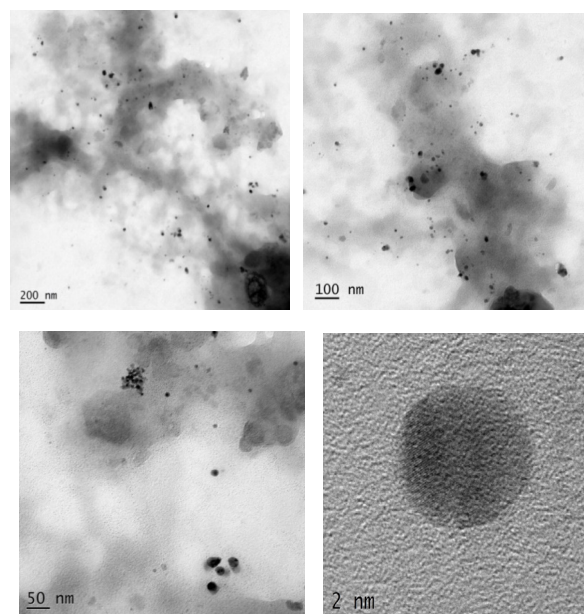


Fig 6: zeta potential distribution graph of (a) 2.5ml extract+AgNO₃ (b) 5ml extract+AgNO₃ (c) 7.5 extract+AgNO₃

TEM ANALYSIS

The grid for the TEM analysis of Agnanoparticles was prepared by placing a drop Nano particle suspension on the C- coated copper grid and allowing the H₂O to evaporate inside a vacuum dryer. The TEM analysis revealed that the AgNPs were predominantly spherical shape. The TEM images were recorded at different magnification to find the individual particles. The obtained AgNPs were observed to be spherical with average size between 10- 30nm.



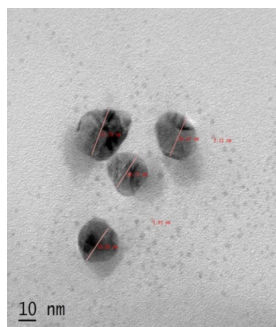


Figure 7: TEM images at different magnification

XRD ANALYSIS

The diffraction intensities were recorded from 10° to 70° at 2θ angles. Figure 8 reveals three intense peaks in the whole spectrum of 2θ value ranging from 10° to 70° , corresponding to three diffraction facets of silver. A number of Bragg reflections corresponding to the (111), (220), (220) sets of lattice planes were obtained, which may be index based on the face centered cubic (FCC) structures of silver nanoparticle. The average size of silver nanoparticles calculated using Scherrer's formula was 26.4084 nm. The silver nanoparticles were spherical in shape. Hence from the XRD pattern it is clear that silver nanoparticles formed using leaves of *coleus aromaticus* were essentially crystalline in nature.

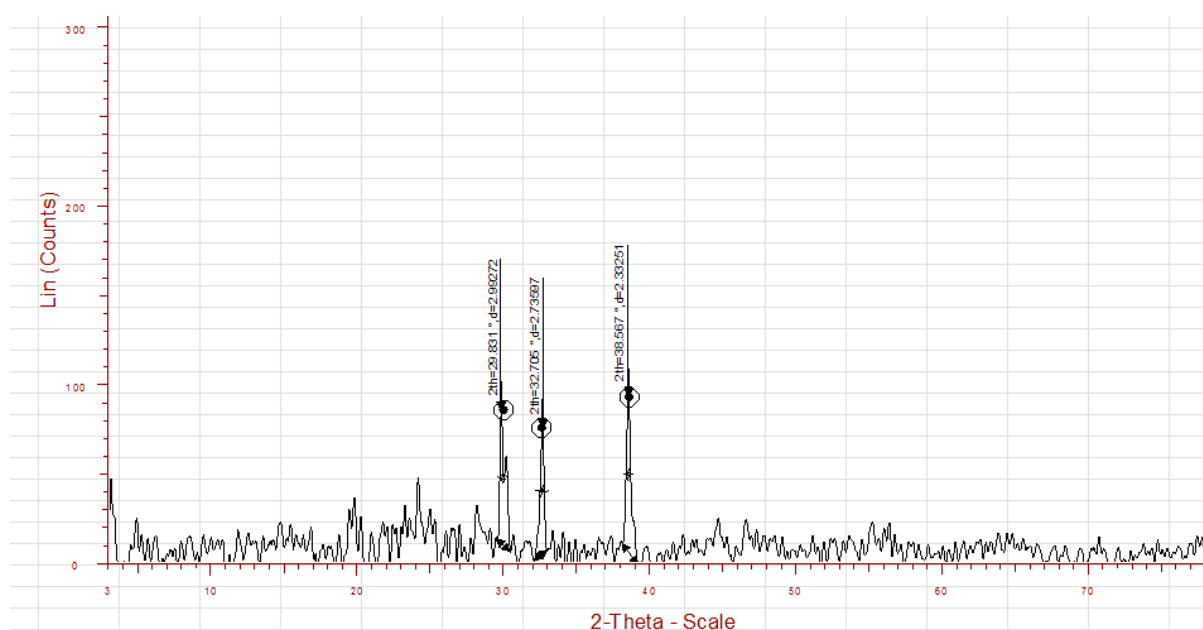


Figure 8: X-ray diffraction pattern of synthesised silver nanoparticles

ANTI BACTERIAL ACTIVITY

The antimicrobial activity of silver nanoparticles (AgNPs) of *coleus aromaticus* leaf extracts were studied and the results are reported. **Table 2** gives the antibacterial activity of AgNPs. The antibacterial property is evaluated using sterile distilled water. Results showed that the AgNPs have considerable antibacterial activity. The antibacterial activity of different solutions containing AgNPs demonstrated that both Gram positive and Gram negative bacteria were inhibited by different solutions with different extents. The activity of these solutions was mainly due to the different amounts of AgNPs formed upon addition of different concentrations of extracts. This was confirmed by the UV as well as FTIR results.

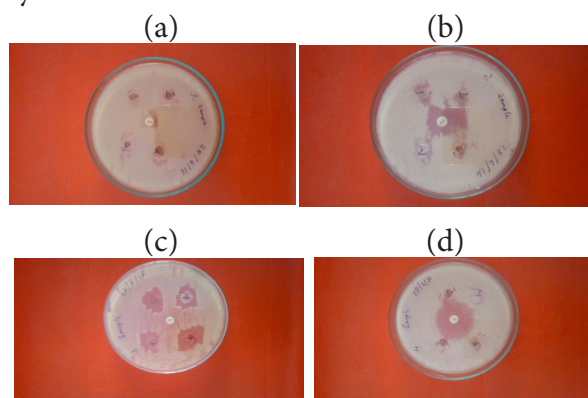


Figure 9: Antimicrobial activities of AgNPs against (a) staphylo coccus (b) salmonella typhi (c) E.coli (d) pseudomonas respectively.

Micro organisms	Zone inhibition (cm)			
	Sample 1	Sample 2	Sample 3	Penicillin
Staphylo coccus	2	2.1	2	1.5
Salmonalla typhi	1.3	1.1	1.5	2
E.coli	1.5	1.6	1.7	1.5
Pseudomonas	1.1	1.3	1.5	2.3

Table 2: Antibacterial activity of silver nanoparticles (AgNPs)

CONCLUSION

In this study, green mediated synthesis of AgNPs by treating silver ions with coleus aromaticus leaf extracts at room temperature without using any harmful chemicals. The fact is confirmed by ultraviolet- visible absorption spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), Dynamic light scattering (DLS), Zetapotential , Transmission Electron microscopy(TEM), X-ray diffraction spectroscopy (XRD). Silver nanoparticles, synthesized by this method were spherical in shape. These nanoparticles showed effective antibacterial activity against Escherichia coli , pseudomonas , salmonalla typhi and staphylo coccus and synthesised silver nanoparticles have considerable effect on staphylo coccus.

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Enhanced photocatalytic activity of Au/TiO₂ and Ag/TiO₂ composite nanoparticles by solar light

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Abstract

Au/TiO₂ and Ag/TiO₂ composite nanoparticles were prepared *via* low temperature hydrothermal route. The synthesized nanoparticles are highly efficient solar photocatalysts and showed higher photocatalytic activity than pure nano TiO₂ and commercial photocatalyst Degussa P25, under sunlight. The activity of different samples in sunlight is in the order Ag/TiO₂ > Au/TiO₂ > TiO₂ > Degussa P25. Gold and silver nanoparticles were prepared by a novel, single step chemical reduction and stabilization employing D-Glucosamine. Synthesized Au/TiO₂ and Ag/TiO₂ composite nanoparticles were characterized by X-ray diffraction (XRD), UV-visible spectroscopy, Raman spectroscopy, BET surface area, Photoluminescence (PL), Field emission scanning electron microscopy (FESEM), EDAX, Transmission electron microscopy (TEM) and Diffused reflectance spectra (DRS) techniques. DRS study showed that Au/TiO₂ and Ag/TiO₂ induces a shift of absorption edge to the visible range and resulted in narrowing of the band gap. The solar photocatalytic efficiency of the synthesized samples were studied by monitoring the photocatalytic degradation of methylene blue and found a drastic increase in the photocatalytic activity of the composite nanoparticles when compared to TiO₂.

Keywords: Nano TiO₂, Solar photocatalysis, Ag/TiO₂, Au/TiO₂, Methylene blue, Dye degradation.

1. Introduction

Semiconductor-metal nanocomposite is an emerging and active area of contemporary science [1]. The catalytic property of the oxide surfaces, modified with the noble metal nanoparticles, is an important aspect in photocatalysis. Many studies have been carried out to improve the photocatalytic activity by reducing the recombination rate by the insertion of noble metals [2-4]. The addition of noble metal into semiconductor can change the photocatalytic process by modifying the semiconductor surface properties [5-7]. Fabricating noble metal/TiO₂ nanocomposites is an effective way to enhance the photocatalytic efficiency of TiO₂ photocatalysts [8-11]. Among

these noble metal/TiO₂ nanocomposites, Au and Ag-modified TiO₂ is of great significance due to its potential applications [12-14].

Due to the wide band gap (3.2 eV) of TiO₂, it is excited only by ultraviolet light to inject electrons into the conduction band and to leave holes in the valence band [15]. Thus, this practically limits the use of sunlight or visible light as an irradiation source in photocatalytic reactions of TiO₂. This has consequent implications for the use of TiO₂ as solar light activated catalyst, because the majority of sunlight consists of visible light and only a 3–5% UV light. More practical applications can be achieved if the photocatalytically active region is extended to

the visible region (400-800 nm) [16]. Hence in the present work, we have made an attempt to synthesize novel TiO_2 photocatalysts with reduced band gap and enhanced activity under solar light for the degradation of methylene blue.

The major challenges in the synthesis of gold and silver nanoparticles are the difficulty in controlling the particle size and the stability of the product. After its formation from corresponding ions by reduction, they need to be stabilized for further use. In this investigation, we adopt a novel strategy for the *in-situ* preparation of gold and silver nanoparticles. In the present study we have synthesized gold and silver nanoparticles in a single step from chloroauric acid (HAuCl_4) and silver nitrate (AgNO_3) using D-glucosamine. We found that D-glucosamine is an excellent reducing agent and can stabilize the colloidal nanoparticles through an electrostatic interaction so that no other stabilizing agents were needed for stabilization of gold and silver nanoparticles. Hence gold and silver nanoparticles stabilized by D-glucosamine were used for the preparation of Au/TiO_2 and Ag/TiO_2 composite nanoparticles to get highly efficient solar photocatalyst. The photocatalytic activity of the synthesized samples under sunlight was studied by the degradation of methylene blue (MB) and compared with pure anatase nano TiO_2 powder and commercial photocatalyst Degussa-P25.

2. Experimental

2.1 Materials

Analytical grade titanium (IV) isopropoxide ($\text{Ti} [\text{OC}_3\text{H}_7]_4$) purchased from Acros Organics was used for the synthesis. Methylene blue was obtained from Rankem and chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), sodium hydroxide (NaOH) and D-glucosamine hydrochloride were purchased from Aldrich chemicals. All these chemicals were used without further purification. Deionized water was used throughout the experiments.

2.2 Synthesis of Gold nanoparticles

Preparation of gold nanoparticles was carried out by mixing 15 ml of 0.2 mM HAuCl_4 , 35 ml of 10 mM D-glucosamine hydrochloride, with

constant stirring for 5 minutes. The color of the solution slowly turned from yellow to wine red, indicating the formation of gold nanoparticles. The formation of nanoparticles was confirmed through absorption spectral analysis and TEM images.

2.3 Synthesis of Silver nanoparticles

Preparation of silver nanoparticles was carried out by mixing 30 ml of 670 μM silver nitrate, 25 μL of 0.25 M sodium hydroxide and 0.2 ml of 10 mM D-glucosamine hydrochloride. The solution slowly turned to bright yellow due to the formation of silver nanoparticles. The formation of nanoparticles were confirmed through absorption spectral analysis and TEM images.

2.4 Synthesis of Au/TiO_2 and Ag/TiO_2

An adequate amount of 60 mM titanium (IV) isopropoxide solution in ethanol was added to the highly dispersed Au nanoparticle solution synthesized by the above method under vigorous stirring for 10 min at ambient temperature to obtain a suspension of Au/TiO_2 composite nanoparticles. The excess solvent (ethanol and water) in the Au/TiO_2 suspension was removed by rotary evaporation until the Au/TiO_2 powder was produced. The powder was hydrothermally crystallized at 180°C for 12 h. After hydrothermal treatment, the powders were filtered, washed with distilled water and dried at 80°C . Ag/TiO_2 also was synthesized using a similar procedure with the use of silver nanoparticles instead of gold nanoparticles. Pure nano TiO_2 powder was also synthesized using this procedure without the addition of silver or gold nanoparticles.

The X-ray diffraction patterns (XRD) of the synthesized samples were obtained on a Bruker D8 Advance Diffractometer using $\text{Cu K}\alpha$ radiation. DRS of the samples were performed using a UV-2450 Shimadzu UV-visible spectrophotometer. The photoluminescence (PL) spectral measurements were made with the synthesized TiO_2 nanoparticles using Shimadzu RF-5301 spectrofluorophotometer at an excitation wavelength of 300 nm and 325 nm for Ag/TiO_2 and Au/TiO_2 respectively. The BET specific surface area of the powders was measured *via* nitrogen adsorption, using a

surface area analyzer (Micromeritics, Gemini, USA). A Jeol JSM 6500F scanning electron microscope was used for FESEM studies. TEM images were taken using a Jeol JEM-3010 transmission electron microscope.

The photocatalytic activity of the synthesized samples was determined by photocatalytic degradation of methylene blue. For a typical photocatalytic experiment 0.1 g of synthesized nano TiO_2 was suspended in 100 ml of 50 ppm aqueous methylene blue solution. The resulting suspension was equilibrated by stirring in the dark for 30 min. To study the photocatalytic degradation under sunlight the methylene blue- TiO_2 suspension was kept under dark and then kept under direct sunlight. The samples were withdrawn at different time intervals and centrifuged at 6000 rpm to remove the TiO_2 powders. The absorbance of methylene blue was measured at 660 nm using a UV-2450 Shimadzu UV-visible spectrophotometer. It was observed that no detectable degradation of methylene blue occurs without TiO_2 or with solar irradiation alone.

3. Results and discussion

Fig.1a. shows the absorption spectrum of solution containing silver nitrate and sodium hydroxide after the addition of glucosamine hydrochloride, recorded at different time intervals and it clearly shows the formation of new bands at 405 nm which is the characteristic plasmon absorption of silver nanoparticles. The intensity of this absorption increases with time and reaches maximum at 30 min. and thereafter there was no considerable increase. This indicates that the formation of silver nanoparticles was completed within 30 min. The formation of silver nanoparticles was confirmed by TEM image (Fig.1c). Fig.1b. is the absorption spectrum of solution containing chloroauric acid after the addition of glucosamine hydrochloride, recorded at different time intervals and it clearly shows the formation of new bands at 523 nm which is the characteristic plasmon absorption of gold nanoparticles. The formation of gold nanoparticles was confirmed by TEM image (Fig.1d). The results clearly show that glucosamine is an excellent capping and stabilizing agent for silver and gold

nanoparticles.

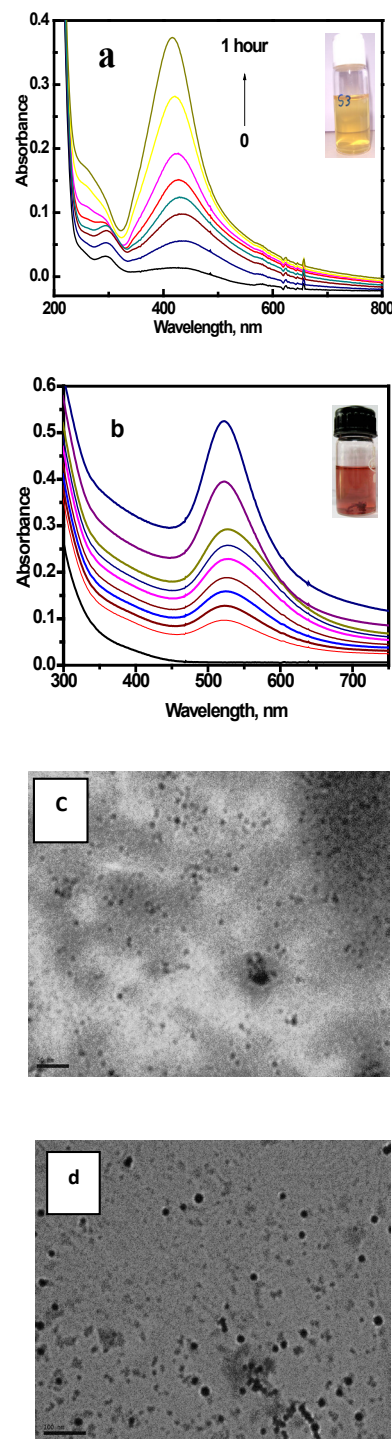


Figure 1 (a) Absorption Spectrum of Silver nanoparticles recorded at different time intervals (inset shows the color photograph of nanosilver) (b) Absorption Spectrum of gold nanoparticles recorded at different time intervals (inset shows the color photograph of nanogold) (c) TEM image of synthesized silver nanoparticles (d) TEM image of synthesized gold nanoparticles

3.1 XRD Analysis

X-ray diffractograms (XRD) of Au/TiO₂, Ag/TiO₂ and unmodified TiO₂ samples are shown in Fig. 2. XRD patterns reveal that the samples show a high degree of crystallinity and the crystalline phase are of typical anatase (JCPDS, No.21-1272). There is slight increase in crystallinity of Au/TiO₂ and Ag/TiO₂ nanoparticles, but no phase change is observed. However, there are no clear peaks showing the presence of silver or gold in the XRD patterns of Au/TiO₂ and Ag/TiO₂, which is due to the low silver and gold content [17,18]. The nanocrystallite size of the synthesized samples was estimated using Scherrer's equation; $D_{\text{XRD}} = 0.9\lambda/\beta \cos\theta$, where D is the crystallite size, λ is the wavelength of X-ray used, β and θ are full width at half maximum intensity (in radian) (FWHM) of XRD diffraction lines and half diffraction angle 2θ , respectively. The crystallite sizes of samples are given in Table 1.

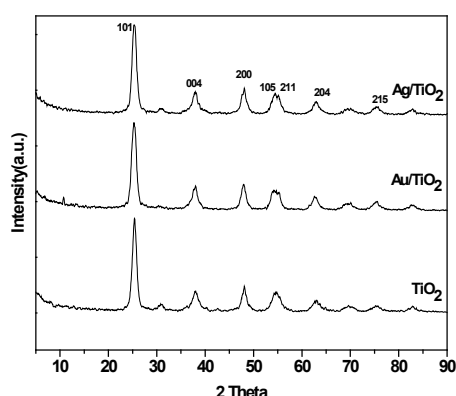


Figure 2 XRD patterns of unmodified TiO₂, Au/TiO₂ and Ag/TiO₂

3.2 Diffused Reflectance spectra results

To investigate optical absorption properties of the synthesized samples the diffuse reflectance absorption spectra (DRS) of unmodified TiO₂, Au/TiO₂ and Ag/TiO₂ were examined in the range 300-750 nm and the results are shown in Fig.3. It is clear from the figure that unmodified TiO₂ nanocrystals has absorption in the UV region and is ascribed to charge transfer from valence band (mainly formed by 2p orbitals of oxide anion) to the conduction band (mainly formed by 3d_{t_{2g}} orbitals of Ti⁴⁺ cation) [19].

The samples Au/TiO₂ and Ag/TiO₂ showed significant absorption in the visible region which is in good agreement with the earlier reports [17,20]. The red shifted photoresponse of Au/TiO₂ and Ag/TiO₂ as observed in the figure may lead to high photocatalytic activity under visible region which helps in the enhancement of photocatalytic activity under sunlight. The broad absorption bands around 450 nm and around 550 nm may be attributed to the absorption of the silver and gold nanoparticles respectively, adsorbed on the surface of TiO₂ particles. [21]

The band gap energies of the synthesized samples were calculated by the equation;

$$E_g = 1239.8/\lambda \quad [22],$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edges in the spectrum. The band gap values are given in table 1 and the values indicate that gold and silver in Au/TiO₂ and Ag/TiO₂ reduced the band gap of TiO₂ nanocrystals. The band gap narrowing was primarily attributed to the substitution of gold and silver nanoparticles which introduced electron states into the band gap of TiO₂ to form a new lowest unoccupied molecular orbital. The shift of absorption edge of TiO₂ to visible range and narrowing of band gap increased the photocatalytic activity of TiO₂ in the visible region.

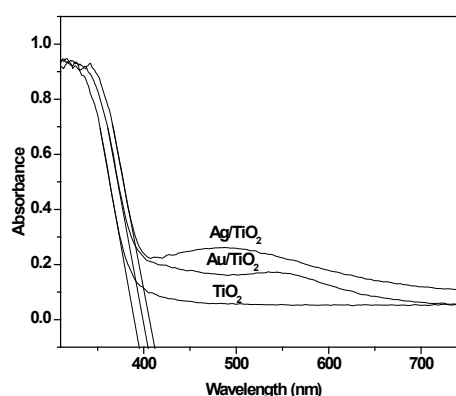


Figure 3 DRS of unmodified TiO₂, Au/TiO₂ and Ag/TiO₂

Sample	Surface area (m ² /g)	Particle size (D _{BET}) (nm)	Crystallite size (D _{XRD}) (nm)	Band gap (eV)
TiO ₂	139.15	10.78	14.18	3.15
Au/TiO ₂	145.94	10.28	14.00	3.07
Ag/TiO ₂	151.59	9.89	13.44	3.01

Table 1 BET surface area, particle size, crystallite size and band gap of unmodified TiO₂, Au/TiO₂ and Ag/TiO₂

3.3 Surface Area Analysis

BET surface areas measured for the synthesized samples are given in table 1 and show that the surface areas of the samples are high compared to earlier reports [23,24]. The average nanoparticle sizes were calculated from BET surface area using the equation; $D_{BET} = 6000/\rho S$, where D_{BET} is the average nanoparticle size (nm), ρ is the powder density (g/cm³), S is the specific surface area (m²/g). The results are shown in table 1 and are comparable with the average nanocrystallite size determined using Scherrer's equation.

3.4 Morphological Analysis

FESEM (Fig. 4a, b and c) and TEM (Fig. 4d and e) images of the TiO₂, Au/TiO₂ and Ag/TiO₂ samples are given in Figure 4. In TEM images, Au and Ag nanoparticles are distinguishable and appear as dark dots on the surface of the TiO₂ particles. The presences of gold and silver particles are also confirmed from EDAX (Fig.5). Also, there is a possibility for gold and silver to be incorporated into the interstitial positions of the TiO₂ semiconductor particles. It is also clear that the crystallinity has been increased which is indicated by the increased crystal size with well-developed faces. This observation is in good agreement with the XRD data given in section 3.1.

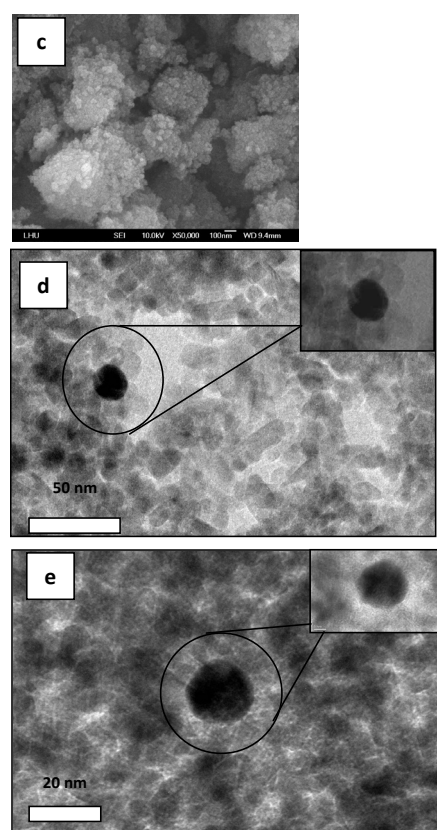
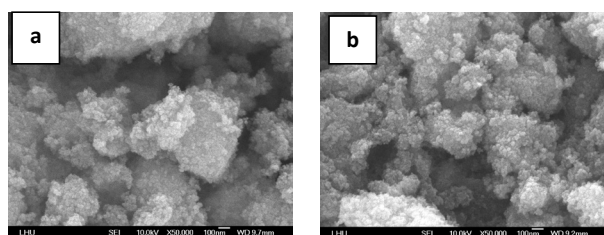
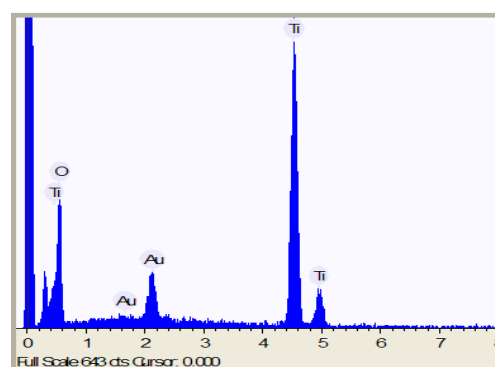


Figure 4 FESEM Images of a) unmodified TiO₂ b) Au/TiO₂ and c) Ag/TiO₂, TEM Images of d) Au/TiO₂ and e) Ag/TiO₂



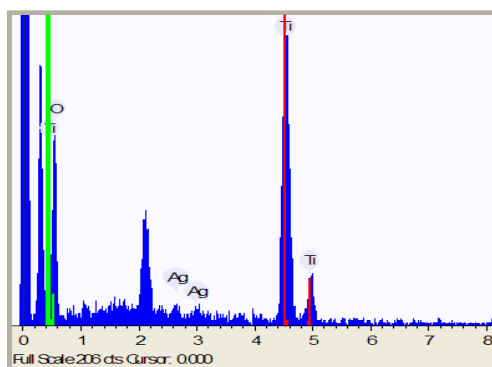


Figure 5 EDAX of Au/TiO₂ and Ag/TiO₂ composite nanoparticles

3.5 Raman Spectra

Fig. 6 shows the Raman spectra of the synthesized nanotitania. The peak positions of unmodified TiO₂, Au/TiO₂ and Ag/TiO₂ (table 2) correspond to the allowed Raman active modes of anatase crystals. The presence of gold and silver nanoparticles on the TiO₂ surface slightly reduce the intensities of the peaks in Au/TiO₂ and Ag/TiO₂ which is in good agreement with the earlier report [25].

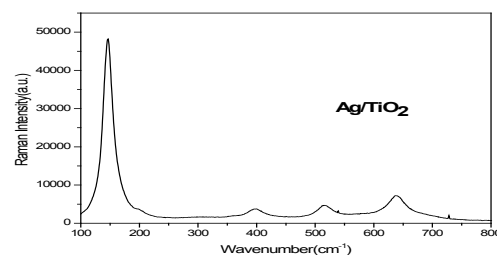
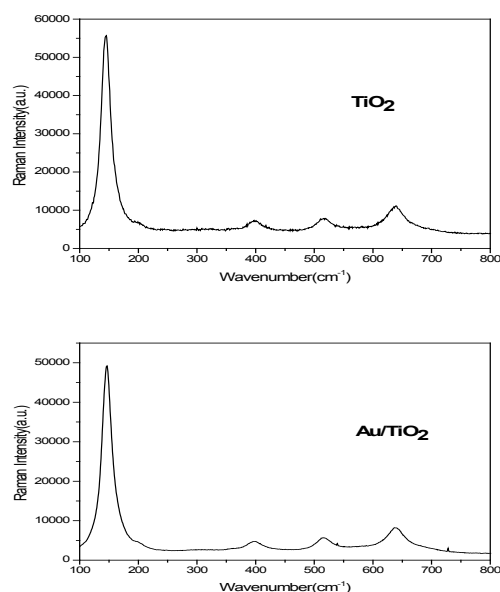


Figure 6 Raman spectra of a) unmodified TiO₂ b) Au/TiO₂ and c) Ag/TiO₂

3.6 Photoluminescence Studies

The photoluminescence emission spectra (PL) of the unmodified and modified nanotitania were studied in the range of 200-600 nm to investigate the separation efficiency of charge carriers and the results are shown in Fig.7. It is evident from the figure that the PL intensity of TiO₂ > Au/TiO₂ > Ag/TiO₂. The lower PL intensity shows that the rate of recombination between electron and holes is low [26]. The electrons are excited from valance band (VB) to conduction band (CB) of TiO₂ under UV irradiation and generate photoexcited electrons and holes. Although gold and silver narrows the band gap of TiO₂ samples, the recombination of electrons and holes are relatively slow which is evident from PL spectra.

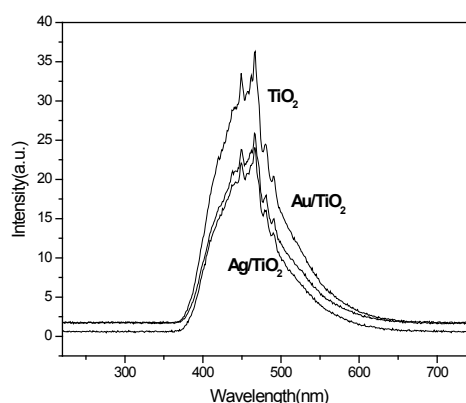


Figure 7 PL Spectra of a) unmodified TiO₂ b) Au/TiO₂ and c) Ag/TiO₂

Sample	E _g	E _g	B _{lg}	A _{lg}	E _g
TiO ₂	145.3358	194.0298	397.2015	516.4179	638.9925
Au/TiO ₂	146.5539	197.0514	399.8338	516.6112	638.1229
Ag/TiO ₂	146.5531	197.8405	399.8338	516.6112	638.1229

Table 2 The wavenumber of the samples (cm⁻¹) obtained from Raman spectra

As is well known, TiO_2 exhibit poor photocatalytic efficiency since the majority of photogenerated charge carriers undergo recombination. In the present system, silver and gold nanoparticles act as electron acceptors and sinks for the charge carriers which will enhance the efficiency of photocatalysis [26,27]. In the case of Au/TiO_2 and Ag/TiO_2 composites, gold and silver nanoparticles play an important role in the interfacial charge transfer and in the decrease in rate of electron-hole recombination. Gold and silver nanoparticles could act as an effective electron scavenger to trap the photo induced electrons and holes of TiO_2 leading to the reduction of electron-hole recombination and thus improving the photocatalytic efficiency. The electrons trapped in gold and silver sites were subsequently transferred to the surrounding adsorbed O_2 . It can be supported by PL emission spectra, which have been widely used to investigate the fate of electron hole pairs in semiconductor particles since PL emission results from the recombination of free carriers [21, 28].

3.7 Photocatalytic activity

To investigate the photocatalytic activity of synthesized samples in solar light, the degradation of MB was studied in presence of TiO_2 , Au/TiO_2 and Ag/TiO_2 nanoparticles under sunlight. For comparison, photocatalytic studies were also performed with commercially available photocatalyst, Degussa P25 and the results are shown in Fig.8. The activity of different samples in sunlight is in the order $\text{Ag/TiO}_2 > \text{Au/TiO}_2 > \text{TiO}_2 > \text{Degussa P25}$. Ag/TiO_2 samples show higher activity than Au/TiO_2 , undoped TiO_2 and Degussa P25. Diffuse reflectance spectra of Ag/TiO_2 samples showed significant absorption in the visible region which enhance the photocatalytic activity in the visible region. The high activity of Ag/TiO_2 samples is mainly attributed to the decrease in band gap (3.15 to 3.01 eV), which leads to the easy excitation of electrons from valence band to conduction band on exposure to visible light. Silver nanoparticles could act as an effective electron scavenger to trap the conduction band electrons of TiO_2 [26]. In Ag/TiO_2 the silver nanoparticles play an important role in the interfacial charge transfer and in the elimination

of electron-hole recombination as is evident from PL spectra, which would be beneficial for the high photocatalytic activity. The activity of unmodified TiO_2 is less because here electrons cannot be excited from valence band to conduction band by visible light irradiation due to the large band gap as calculated from DRS (3.15 eV). In this case an ultraviolet irradiation is required for the excitation of electrons from valence band to conduction band to carry out photocatalysis, which accounts for only small fraction of the solar light. Also the efficiency of the photocatalysis depends on the effectiveness of the photocatalytic process in transferring the photoinduced e^-/h^+ pair from the particle volume to the particle surface and subsequently to the surface-adsorbed species. In un modified TiO_2 there is no intermediate level to trap the electron and the recombination possibility of electrons and holes is enhanced and the free electron or holes available for the photocatalysis is less, subsequently the efficiency of photocatalysis also is less.

It is well known that it is the anatase polymorph rather than the brookite or rutile polymorph that has the highest photocatalytic activity. The most active commercially available photocatalyst (Degussa P25) has an anatase content of 75% and 25% of rutile content [29]. From the XRD pattern it is evident that the synthesized samples (TiO_2 , Au/TiO_2 and Ag/TiO_2) are purely anatase and hence it shows higher activity than Degussa P25.

The synthesized Au/TiO_2 and Ag/TiO_2 samples are highly efficient photocatalysts than Degussa P25 and unmodified TiO_2 as is evident from the MB degradation studies. Also silver and gold could replace artificial UV light irradiation by sunlight. Hence it is clear that Ag/TiO_2 and Au/TiO_2 can give highly efficient photocatalysis under sunlight.

In addition to higher photocatalytic activity, the hydrothermally synthesized TiO_2 samples are easier to separate from the aqueous media than Degussa P25. Degussa P25 forms a milky white turbid suspension in aqueous media. Though the synthesized samples have equal or less particle size they do not form turbid suspension. Also the synthesized catalysts settle faster and it is easier to separate from the reaction mixture

by centrifugation. This enabled recyclability of the synthesized nanophotocatalysts after centrifugation at the end of each photocatalytic cycle and the recycled catalyst was found efficient and stable for more than six cycles.

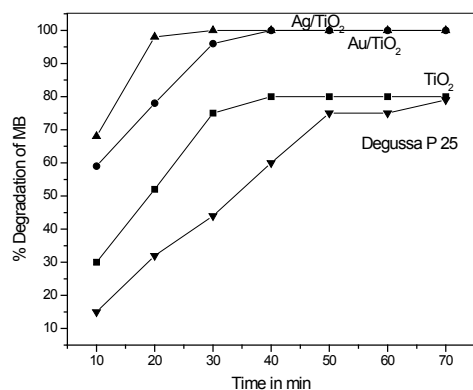


Figure 8 Photocatalytic activities of TiO₂, Au/TiO₂, Ag/TiO₂ and Degussa P 25 under sunlight.

Conclusions

Au/TiO₂ and Ag/TiO₂ anatase nanocrystals with enhanced photocatalytic activity under solar irradiation have been successfully synthesized

by low temperature hydrothermal route. Gold and silver nanoparticles used for doping were prepared by simultaneous chemical reduction and stabilization employing D-glucosamine, without any additional stabilizing agent. The hydrothermally synthesized TiO₂ samples showed higher photocatalytic activity under sunlight than the commercially available photocatalyst Degussa P25 and could completely degrade the methylene blue by sunlight irradiation. Also the synthesized catalysts settle faster and it is easier to separate from the reaction mixture which promotes the reusability of these photocatalysts. Decrease in band gap in Au/TiO₂ and Ag/TiO₂ samples by the formation of an intermediate level is the major reason for the high photocatalytic activity of these samples under sunlight. The photocatalytic activity of Ag/TiO₂ is better than Au/TiO₂. The present study suggests that Au/TiO₂ and Ag/TiO₂ can be used for the development of an environmentally sustainable photocatalytic treatment process for the degradation of organic pollutants using sunlight in place of an artificial light.

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Spectroscopic investigations and molecular docking study of morpholine

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Abstract

The vibrational spectra and corresponding vibrational assignments of morpholine is reported. The chemical reactivity descriptors are calculated theoretically. Molecular docking studies suggest that the compound might exhibit inhibitory activity against tyrosine-protein kinase JAK2. NBO, MEP and frontier molecular orbital analysis are also discussed.

Keywords: morpholine; DFT; docking; NBO.

Introduction

Morpholine is a six membered heterocyclic compound which features both amine and ether functional groups and its derivatives have several industrial applications, such as corrosion inhibitor, optical bleaching agent, and in textile solvent to dissolve cellulose, and fruit or vegetable preservation/glazing agent. Substituted morpholine derivatives are the core of various natural and biologically active compounds and have important applications in pharmaceutical field [1].

Computational details

The quantum chemical calculations have been carried out to find the structure of the molecule (Fig.1), vibrational wavenumbers, NBO], MEP, frontier molecular orbitals, NLO properties using B3LYP/6-311++G (5D, 7F) by Gaussian09 software [2] and Gaussview software [3] and the IR and Raman spectra are downloaded from SDBS data base [4]

Results and discussion

Table 1. Calculated scaled wavenumbers, observed IR, Raman bands and assignments

B3LYP/6-311G (5D, 7F) $\nu(\text{cm}^{-1})$	Raman $\nu(\text{cm}^{-1})$	IR $\nu(\text{cm}^{-1})$	Assignments
3430	3368	3327	νNH
2986	-	-	νCH_2
2995	-	-	νCH_2
2946	2947	2944	νCH_2
2910	-	2912	νCH_2
2894	-	-	νCH_2
2889	-	-	νCH_2
2878	2872	-	νCH_2
2823	2820	2830	νCH_2

1498	-	-	νCH_2
1489	-	-	νCH_2
1483	1485	-	νCH_2
1473	-	-	δNH
1458	1460	1459	δCH_2
1370	-	1375	δCH_2
1365	-	-	δCH_2
1351	-	1352	δCH_2
1335	1332	1330	δCH_2
1263	-	1263	δCH_2
1219	1220	-	δCH_2
1213	-	1211	δCH_2
1193	-	1191	νCN
1131	1145	1136	δCH_2
1084	-	1090	δCH_2
1070	1073	1065	νCO
1042	-	-	δCH_2
1035	1033	1032	$\nu\text{CN}, \delta\text{CH}_2$
983	-	-	νCN
862	-	-	δCH_2
847	-	845	$\delta\text{CH}_2, \nu\text{CC}$
823	826	819	νCO
761	-	-	τCH_2
608	-	604	γNH
509	-	-	τCH_2
464	475	-	τCH_2
415	421	-	τCH_2
269	272	-	τCH_2
253	-	-	$\tau\text{CH}_2, \tau\text{CN}$
61	-	-	$\tau\text{CH}_2, \tau\text{CO}$

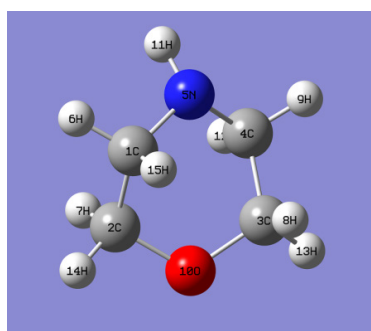


Fig.1

IR and Raman spectra

The vibrational assignments are tabulated in table 1. The vibrations of the CH_2 group, stretching and deformation modes are expected in the regions, 2800-3000 cm^{-1} and

1450-800 cm^{-1} according to literature [5] and in the present case, these modes are observed at 2944, 2912, 2830 cm^{-1} in the IR spectrum, 2947, 2872, 2820 cm^{-1} in the Raman spectrum, 2986-2823 cm^{-1} (DFT) (stretching) and 1459, 1375, 1352, 1330, 1263, 1211, 1136, 1090, 1032 cm^{-1} in the IR spectrum, 1485, 1460, 1332, 1220, 1145, 1033 cm^{-1} in the Raman spectrum, in the range 1498-862 cm^{-1} (DFT) (deformation modes). The C-N and C-O stretching modes are assigned at 1193, 983 cm^{-1} and 1070, 823 cm^{-1} theoretically as expected [5]. The NH stretching mode is observed at 3322 cm^{-1} in the IR spectrum and 3368 cm^{-1} in the Raman spectrum and the NH deformation mode is assigned at 1473 cm^{-1}

theoretically. The vibrational assignments are given in table 1.

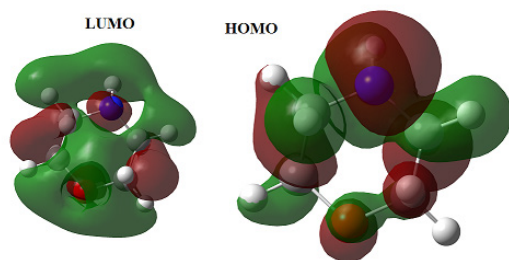


Fig.2

Natural bond orbital analysis

There occurs an intra-molecular hyper conjugative interaction C_1-C_2 from N_5 of $n_1(N_5) \rightarrow \sigma^*(C_1-C_2)$ which increases ED (0.02962e) and weakens the respective bonds C_1-C_2 leading to stabilization of 5.55 kJ/mol and a strong intra-molecular hyper conjugative interaction C_1-C_2 from O_{10} of $n_1(O_{10}) \rightarrow \sigma^*(C_1-C_2)$ which increases ED (0.02962e) and weakens the respective bonds C_1-C_2 leading to stabilization of 2.78 kJ/mol. Another hyper conjugative interaction of C_3-C_4 from O_{10} of $n_2(O_{10}) \rightarrow \sigma^*(C_3-C_4)$ which increases ED (0.01975e) and weakens the respective bonds C_3-C_4 leading to stabilization of 2.24 kJ/mol. The NBO analysis describes the bonding in terms of the natural hybrid orbital $n_2(O_{10})$, which occupy a higher energy orbital (-0.27524a.u.) with considerable p-character (99.99%) and low occupation number (1.93921) and the other $n_1(O_{10})$ occupy a lower energy orbital -0.54534a.u.) with p-character (52.09%) and high occupation number (1.96666). The NBO analysis also describes the bonding in terms of the natural hybrid orbital $n_1(N_5)$, which occupy a higher energy orbital (-0.24929a.u.) with considerable p-character (90.06%) and low occupation number (1.91925). Thus, a very close to pure p-type lone pair orbital participates in the electron donation to the $n_1(N_5) \rightarrow \sigma^*(C_1-C_2)$, $n_1(O_{10}) \rightarrow \sigma^*(C_1-C_2)$ and $n_2(O_{10}) \rightarrow \sigma^*(C_3-C_4)$ interactions in the compound.

Frontier molecular orbital and molecular electrostatic potential map

The HOMO and LUMO plot of the title compound is given in Fig.2. The HOMO and LUMO is delocalized over the entire molecule.

Using HOMO and LUMO orbital energies, the ionization energy and electron affinity can be expressed as: $I = -E_{\text{HOMO}}$, $A = -E_{\text{LUMO}}$. The hardness η , electronegativity χ and chemical potential μ are given by the following relations: $\eta = (I-A)/2$ and $\mu = -(I+A)/2$, where I and A are the first ionization potential and electron affinity of the chemical species [6]. The energies of the HOMO, LUMO orbital and energy gap $E_{\text{HOMO}} = -8.358\text{eV}$, $E_{\text{LUMO}} = -1.150\text{eV}$, energy gap = 7.208eV. The ionization potential (I), Electron affinity (A), global hardness (η), chemical potential (μ) and global electrophilicity ($\omega = \mu^2/2\eta$) are 8.358, 1.150, 3.604, -4.754, 3.135 respectively. MEP mapping in quantum chemistry is a valuable tool not only used to visualize the reactive sites in a compound but also helpful in biological recognition studies as well as hydrogen bonding interactions [6]. Optimized molecular structure was used for generation of MEP surface plots of the title compounds and mapped with rainbow colour scheme (electron rich regions represent with red color, while electron poor regions represent with blue colour). MEP and surface analysis diagram of title compounds showed in Fig.3, negative regions are mainly localized over N and O atoms, it is represent with red colour in rainbow color scheme (electrophilic attack) while the maximum positive regions are localized over hydrogen atoms (nucleophilic attack).

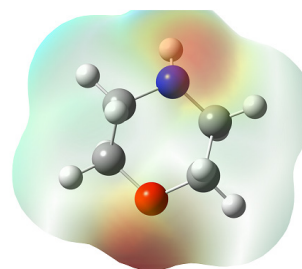


Fig.3

Molecular docking

Based on the structure of a compound, PASS (Prediction of Activity Spectra) [7] is an online tool which predicts different types of activities. PASS analysis of the title compound predicts Phobic disorders treatment activity with probability to be active (Pa) value of 0.937. Morpholins and their derivatives

are used therapeutic agents prominently in anxiety disorder, obsessive-compulsive disorder, panic disorder and social phobia [8,9]. High resolution crystal structure of myeloproliferative disorders protein tyrosine-protein kinase JAK2 was downloaded from the protein data bank website (PDB ID: 5AEP). All molecular docking calculations were performed on Auto Dock-Vina software [10] and as reported in literature [6, 11]. The 3D crystal structure of tyrosine-protein kinase JAK2 was obtained from Protein Data Bank. Amongst the docked conformations, one which binds well at the active site was analysed for detailed interactions in Discovery Studio Visualizer 4.0 software. Amino acids Glu898, Gly861 forms H-bond with the title compound. The docked ligand title compound forms a stable complex with tyrosine-protein kinase JAK2 and gives a binding affinity (ΔG in kcal/mol) value of -5.0 kcal/mol. These preliminary results suggest that the compound might exhibit inhibitory activity against tyrosine-protein kinase JAK2. However biological tests need to be done to validate the computational predictions.

Conclusion

The observed experimental and theoretical wavenumbers are assigned and electrophilic and nucleophilic sites in the molecule are identified. . PASS analysis of the title compound predicts Phobic disorders treatment activity. The docked ligand title compound forms a stable complex with tyrosine-protein kinase JAK2 and gives a binding affinity value of -5.0 kcal/mol.

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River Pollution Studies in the Capital City of Kerala: Emerging Concerns

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ABSTRACT

Almost all rivers flowing through the capital cities of various states in India were reported for different types of pollution. The Kerala State is not an exception in this. The Karamana river, the 17th largest out of the 44 rivers of Kerala State, has a length of 68 Km and is flowing through the State capital with an average annual stream flow is 836Mm³ of freshwater debouching into the Arabian Sea. The total watershed area of Karamana basin is 690Km². The textural and heavy metal studies were performed in the river sediments collected from seventeen stations at regular intervals during pre-monsoon, monsoon and post-monsoon seasons. The sampling sites were fixed on such a way that the results arrived through various types of examinations of sediments would reflect the ground realities of environmental deterioration of the fluvial regime. Statistical tools [Contamination factor (CF) and Pollution Load Index (PLI)] were used to get an overall idea about the heavy metal pollution in the riverine environment.

Keywords: Heavy metal Pollution, Karamana River, Textural analysis, Contamination factor, Pollution load index

1. INTRODUCTION

Rivers have been the foci of civilization since the dawn of recorded history or long before. By one definition, a river is a relatively large volume of water moving within a visible channel, including subsurface water moving in the same direction and the associated floodplain and riparian vegetation (Naiman *et al.*, 1992). A river network comprises the master channel, tributaries and distributaries. The interfluvies and, the bed and banks constitute important sources for river sediments. Running water, capable of eroding and transporting materials, is derived mainly from precipitation. By and large a river basin is an ideal unit of land surface

and, it is perhaps the most suitable frame of reference for capturing and documentation of data on the biosphere.

Reports indicate that many of the river basins of Kerala are degrading at faster rates consequent to various kinds of anthropogenic activities. The scenario is very severe in those basins, which host industrial or urban agglomerations. In the light of the above, an attempt has been made in this investigation to document the state of environment of the Karamana river basin of southern Kerala – which host the capital town Thiruvananthapuram. Knowledge of textural characteristics and geochemical composition

of sediments is very significant in the overall understanding of an aquatic environment. This paper deals with the geochemical characteristics of the surface sediments of the Karamana river. An attempt has also been made to compare the geochemical attributes of these systems with the other major Indian rivers.

Geochemical studies of aquatic sediments have increasingly being carried out in the last few decades, owing to the need of an understanding of the pathways of toxic contaminants that causes disastrous effect to our environments. Sediments are both carriers and potential sources of natural geochemical constituents derived principally from rock weathering. However, over the 200 years following the beginning of industrialisation, huge changes in the global budget of chemical signals, particularly of toxic contaminants, have occurred challenging the natural regulatory systems which took millions of years to evolve. In the early seventies, following the catastrophic events of cadmium and mercury poisoning, sediment associated toxic elements; its carrier phases and the natural regulating mechanisms have received wide public attention. Since then, exhaustive research has been carried out in the world's major rivers to monitor the contaminant discharges and its behaviour under different geochemical set ups. Gibbs (1977) through granulometric partitioning studies opined that the heaviest enrichment of metal occurs in the finer fractions, ranging in diameter from 0.20 μm to 20 μm . The level variability of elements and its various forms in sediments are reflections of the various factors, which govern quality of the environment. These geochemical signals are introduced in aquatic environments either in solid/colloidal insoluble forms by water and wind.

2. STUDY AREA

The Karamana river basin lies between 8° 20' to 8° 45' North latitudes and 76° 50' to 77° 15' East longitude and is located in the Thiruvananthapuram district of Kerala state. The major river draining through this watershed is the Karamana river, which has a length of 68 Km and has a total yield of 836 Mm³ of freshwater. The total watershed area of Karamana basin

is 690Km². Karamana river originates from Chemmunjimottai (Nedumangad hills) at an elevation of about 1717 m above msl and flowing through the State capital and finally merges into the Arabian Sea near Thiruvallom. The general elevation ranges from 310m in the upper region, 60m in the middle region and less than 4m in the lower region. The broad landforms in the upper region of the basin include high hills and low hills with isolated hillocks. The middle region consists of lateritic mounds and isolated hillocks. Gently sloping coastal landforms are seen in the lower region.

3. SAMPLING AND ANALYSIS

The sampling has been carried out at regular intervals during premonsoon, monsoon and postmonsoon seasons. The sampling sites (Fig. 1) were fixed on such a way that the results arrived through various types of examinations of sediments would reflect the ground realities of environmental deterioration of these fluvial regimes. The indiscriminate mining for river sand, clays and in some cases for precious stones like chrysoberyl are reported at many places in the basin. One sample (sample 17) from the river was collected from the river mouth zones close to barrier beach. This is to know about the textural and geochemical attributes of the marine influenced zones of these basins.

The sediment samples were obtained using a stainless steel van Veen grab. All the samples were carefully transferred into neatly labelled polythene bags and were brought to laboratory and analysed for various parameters. Utmost care was taken not to contaminate the samples during collection and handling. A portion each of the sediment samples collected from the Karamana river were dried and powdered well for geochemical analysis. Mud fraction was separated from the respective subsamples using 230 mesh (63 μm) ASTM sieve. The samples were also dried and powdered for further analysis. The sand, silt and clay content of the bulk sediments were determined following pipette analysis

A known quantity of the well-powdered, bulk sediments and mud fractions were digested with HF-HNO₃-HClO₄ acid mixture using standard procedures for the preparation of solution 'B'.

From the solution 'B', the amount of heavy and trace metals such as Fe, Mn, Zn, Pb, Cu, Cr and Cd were determined using a double beam atomic absorption spectrophotometer (Model GBC 932) following the method suggested by Rantala and Loring (1975). The precision and accuracy of the heavy metal estimation were checked against two USGS standard rock samples. All the metal values were in agreement with the published values of Rantala and Loring (1975) and Flanagan (1976).

4. RESULTS AND DISCUSSION

4.1. Geochemistry of sediments

Information on the geochemical constitution of sediments and various size fractions is utmost essential for the better understanding of the pathways of toxic contaminants from land to sea. Thus, sediments can be considered as a bank of environmental knowledge. Furthering of the geochemical investigations became evident with the realisation of the importance of chemical elements for the welfare of man and ultimately the progress of nation at large. Table 1 depicts the sediment coded geochemical data in terms of heavy and trace metals in Karamana river during premonsoon, monsoon and postmonsoon seasons.

4.2. Heavy metals

Heavy metals are those with density value greater than 5 gm/cm³. The term trace metal is used when the concentration of metals in a system is less than 0.1%. Heavy metals persist in the aquatic environment for extended periods of time and concentrate in sediments under favourable conditions. River bed sediments act as sink for heavy metals and they play a vital role in changing the environmental matrix of the system. About 97% of the mass transport of metals to the world oceans from terrestrial environments (Gibbs, 1977) is associated with river sediments. The metal contribution from Indian rivers to the global supply of sediments to the oceans is about 20% (Subramanian, 2000). A variety of factors such as basin geology, physiography, chemical reactivity, lithology, mineralogy, hydrology, vegetation, land use pattern and biological productivity regulate the metal load of a river system (Garrels *et al.*, 1975). Exhaustive researches have been carried

out the world over to monitor the heavy/trace metal discharges into fluvial regimes. Several statistical tools are also employed to assess the pollution load in more meaningful way. The present investigation also provides information on the heavy metals in the sediments of Karamana river.

4.2.1. Iron (Fe) and Manganese (Mn)

Iron and manganese geochemistry in aquatic environments have received attention in the world's scientific scenario owing to the need for understanding the pathways of the toxic contaminants which cause disastrous effects to organisms (Forstner and Wittman, 1983). Iron is one of the most redox-sensitive and common heavy metal known to human beings. The distribution and concentration of iron have a strong bearing on the dispersal pattern of toxic elements like Cr, Cd, Pb, Zn, etc., in the aquatic environments. In most environments, iron and manganese transfer primarily through particulate phase. Particulate Fe and Mn forms deposits in sediment as silicate phases, inorganic/oxide/hydroxide forms, organometallic complexes, etc (Gibbs, 1977). Under oxidising conditions, Fe/Mn forms co-precipitate and scavenge a substantial amount of trace metals dissolved in water. On the other hand, under reducing conditions, the sorbed trace metals will be desorbed back to the overlying waters through interstitial waters (Forstner and Wittman, 1983; Mance, 1987; Klomp, 1990; Padmalal, 1992, Badarudeen, 1997). Iron plays an important role in aquatic systems as a nutrient and as a modulator of the impact of other substances, such as bioavailable phosphorus and trace metals (Hutchinson, 1967; Wetzel, 1975).

The concentration of Fe and Mn in the bulk sediment of the Karamana river is furnished in Table 1. Fig. 2 shows the downstream variation of these elements along the course of the river. The concentration of Fe in the bulk sediments Karamana river varies from 1.44%-2.78%(avg. 2.19%) during premonsoon, 1.56%-2.89%(avg. 2.19%) during monsoon and 1.11%-2.6% (avg. 1.76%) during postmonsoon periods. The interrelationship of Organic carbon and the heavy metals and iron with other heavy metals

during different seasons is shown in table 3. A comparative evaluation of Fe in the sediments of Karamana river (annual mean = 2.05%) with that of other Indian rivers reveals that it is very near to the Indian average (2.9%, Subramanian *et al.*, 1985) and also similar to that of Ganges (2.16%) and Brahmaputhra (2.9%) [Table 2].

Like Fe, the metal Mn also exhibits wide variation in its concentrations in the bulk sediments of the Karamana river. The average concentration observed in Karamana river are: 108.49ppm (range: 24.6-190.8ppm) 92.82ppm (range: 72-149ppm) and 78.24ppm (range: 62-101ppm) during premonsoon, monsoon and postmonsoon period respectively. C-org has also an effective role in tapping Fe. The positive correlation between iron and manganese (Table 3) reveals atleast a portion of that these two metals are co-precipitated as insoluble ferric manganic hydrate. Co-precipitation is favoured by negatively charged hydrous manganese oxides in colloidal form (Rankama and Sahama, 1950; Hirst, 1962; Padmalal and Seralathan, 1993) with a consequent affinity for cations. The metals Fe and Mn get complexes with organic compounds in the riverine environments (Fe more effectively than Mn) and are considerably in the organic materials. The positive correlation of Fe with C-org. supports this view (Table 3). Increased association of metals especially of Fe and Mn with mud fraction (fine grained sediments) is well advocated by several authors (Seralathan, 1987; Nair *et al.*, 1990).

4.2.2. Trace elements (Zn, Pb, Cu, Cr and Cd)

The environmental impact of certain metal species may be more important than the total metal concentration and their cumulative effects. (Forstner and Wittmann, 1983). The speciation pattern depends on the geochemical behaviour of the metal in regard to the physico-chemical characteristics of water and sediment. Rapid urbanization, large scale industrialisation and uncontrolled sprawling of settlements around many coastal areas and cities/townships near to rivers have brought up pollution threats to the surrounding aquatic regimes. The concentration of various trace elements in the sediments of Karamana river is given in Table 1, and their variations with distances are

presented in Fig. 2.

4.2.3. Zinc (Zn) and Lead (Pb)

In the present study, the annual average concentration of Zn in the bulk sediments of the Karamana river is 82.09 ppm. The concentration of Zn varies from 57.4 to 129.9ppm (avg. 90.71ppm), 60 to 102ppm (81.97ppm) and 44-98ppm (avg. 73.59ppm) respectively during premonsoon, monsoon and postmonsoon periods. Zinc is classified as a borderline metal, meaning that it forms bonds with oxygen as well as nitrogen and sulfur donor atoms. Under aerobic conditions, Zn^{2+} is the predominant species at acidic pH, but will be removed as $Zn(OH)_2$ at pH 8-11 (Vymazal, 1985). Anaerobic conditions lead to the formation of ZnS regardless of pH within the range 1-14. Samanidou and Fytianos (1987), working on two rivers in northern Greece, reported that zinc partitioned primarily into the sulfide and Fe-Mn hydrous oxide fractions of the sediments under different geochemical set ups. Zinc binds readily with many organic ligands, particularly in the presence of nitrogen or sulphur donor atoms. Stability constants for zinc/humic acid complexes are variable, and hence the fate of zinc will vary among waterways, depending on the type of humic material present in the system a feature established by Samanidou and Fytianos (1987).

Lead varies considerably in Karamana river. In bulk sediments of Karamana river, the values ranges from 6.77 to 9.1 (avg. 8.07ppm) during premonsoon, 6.32 to 11.4 ppm (avg. 7.82 ppm) during monsoon and 16-8.16 ppm (avg. 7.47ppm) during postmonsoon. Table 2 shows the comparative evaluation of the annual mean of Pb in Karamana river with that of other rivers of India. And, it is noted that the values of present study (Karamana = 7.79 ppm) is lower than that of the major rivers of India like Ganges (25 ppm), Brahmaputhra (13 ppm), Godavari (13 ppm) and Mahanadi, (60 ppm). Mudroch and Duncan (1986) showed that lead in the Niagara river (Canada) preferentially bound to the smallest size fractions of the sediment. This has been systematically by many other studies as well. These observations reiterate the need for monitoring smallest fractions of sediments

to obtain an accurate picture of potential Pb contamination in aquatic environments. Lead typically complexes with sulphides and Fe-Mn hydrous oxides in sediments. In one study of a Greek river, it is estimated that over 50% of sediment-bound lead was associated with these two components (Samanidou and Fytianos (1987). Lead-carbonate complexes are common only in surficial sediments (Purchase and Fergusson, 1986) whereas lead sulfide confined to anaerobic sediments only. Lead typically desorbs from sediments and suspended solids in estuaries under high saline conditions (Ferrari and Ferrario, 1989).

4.2.4. Chromium (Cr) and Copper (Cu)

Chromium occurs in the earth's crust at an average concentration of 100 ppm, principally as minerals in the chromite spinel group. Granitic rocks hold comparatively low amount of Cr (avg. 20 ppm) than basaltic rocks (220 ppm). Sandstones and shales account for 35 ppm and 120 ppm of Cr, respectively (McGrath and Smith, 1990).

The concentrations and averages of Cr in the bulk sediments of Karamana river are: 2.04-3.23 ppm (avg. 2.53 ppm), 1.88-2.83 ppm (avg. 2.2 ppm), and 1.8-2.23 ppm (avg. 2.07 ppm). Samanidou and Fytianos (1987) studied the partitioning of chromium in different fractions in river sediments of northern Greece. They found that a substantial portion of Pb is associated with organic sulphides and Fe-Mn hydrous oxide phases. This partitioning did not change in either the freshwater part of the rivers or their in estuaries. Volatilization, photolysis and biotransformations do not appear to be so important processes in the case of chromium. It should be pointed out that the amount of work done on the environmental chemistry of chromium compounds is relatively small and that very little known about organic complexation and the subsequent fate of these compounds (Moore, 1991).

In Karamana river, the Cu concentration in premonsoon, monsoon and postmonsoon are: 0.92-2.03 ppm (avg. 1.37 ppm), 0.93-1.95 ppm (avg. 1.41 ppm) and 0.66-1.86 ppm (1.43 ppm) in bulk sediments, with an annual average of 2.27 ppm. Copper shows a tendency to form

complexes with inorganic and organic ligands. In fact, in freshwater, at circumneutral pH most of the inorganic copper in solution forms complexes with carbonate, nitrate, sulphate and chloride. In some freshwaters, more than 90% of total Cu may be bound to humic acids (Mantoura et al., 1978). Such a relation is noted in Karamana as well.

4.2.5. Cadmium (Cd)

Cd pollution in aquatic sediments has been rapidly increasing in recent decades as a result of the increasing consumption of this metal by industries. Unlike Pb, Cu and Hg, which have been utilised for centuries, Cd has been widely used only in this century. More than half of our Cd ever used in industries was produced in the last 20 Years (Hutton, 1987). Cd reaches the aquatic environments mainly from the mining and smelting of Cd and Zn, atmospheric pollution from the mining and smelting of Cd and Zn, atmospheric pollution from metallurgical industries, the disposal of wastes containing Cd, (such as incineration of plastic containers and batteries) and burning of fossil fuels (Hutton, 1982). Average concentration of Cd in the earth's crust is estimated to be 0.1 ppm (Bowen, 1979). The metal Cd is closely associated with Zn in its geochemistry: both elements have similar ionic structure and electronegatives and both of them are strongly chalcophile although Cd has a higher affinity for S than Zn.

In the bulk sediments of Karamana river, the concentrations of Cd are: premonsoon = 0.14-0.26 ppm (avg. 0.18 ppm), monsoon = 0.1-0.26 ppm (avg. 0.18 ppm) and postmonsoon = 0.14-0.4 ppm (avg. 0.19 ppm) in bulk sediments. The analysis of the relative abundance of Cd in the riverine environments reveals that a considerable amount of Cd is associated with finer sizes. It is due to the increased surface area of the finer particles, and the presence of trace metal scavenging clays, Fe-Mn complexes and colloidal humic materials.

4.3. Heavy metal accumulation in riverine sediments

Metal pollution in riverine environment is usually caused by land runoff, mining activities, dredging activities and anthropogenic inputs.

Sediment in such affected domains not only records its history, but also indicates the degree of pollution (Sahu and Bhosale, 1991). The mechanism of accumulation of pollutants in the sediments is controlled strongly by the nature of the substrate as well as the physico-chemical conditions causing dissolution and precipitation. The degree of contamination of aquatic sediments was quantified earlier by comparing the elemental concentrations with uncontaminated natural background levels (Forstner and Muller, 1973; Nikofova and Smirnova, 1975). Another method is the one established by Tomlinson *et al.*, (1980), they employed a simple method based on Pollution Load Index (PLI), to assess the extent of pollution by heavy metals in the aquatic environments.

Although concentration levels of heavy metals in the riverine and estuarine sediments of estuarine Kerala rivers have been reported earlier by many researchers (Padmalal, 1992 and several others), the degree of metal pollution has not been quantitatively evaluated using these statistical tools. In the present study, an attempt has been made to use these statistical tools (Contamination factor and Pollution Load Index) to get an overall idea about the heavy metal pollution of Karamana basin. Data on the concentration levels of heavy metals of the riverine bulk sediments were calculated for each sampling stations, following the method suggested by Forstner and Muller (1973). The contamination factor (CF) was obtained from the equation:

CF = Metal concentration in polluted sediment / Background value of the metal (Average shale)

Data on the concentration levels of heavy metals (Fe, Zn, Pb, Cu, Cr and Cd) of riverine sediments of study area with their contamination factor (yearly average) are given in Table 4. While computing CF of sediments of the study region, world average concentration of these elements reported for shale (Turkian and Wedephol, 1961) were taken as the background values.

In Karamana river the stations like Karamana, Vilavoorkkal and Kundamonkadavu are showing higher concentration of these metals.

Concentration of these heavy metals in the sediments is much higher compared to world average concentration of shale samples (Turekian and Wedephol, 1961). This is reflected in relatively higher contamination factor (>1) in sediments of study region which can be attributed to their incorporation by anthropogenic inputs such as agricultural drains, domestic sewage, mining activities and land run-off.

Pollution load index (PLI) was calculated using the equation:

$$PLI = n\sqrt{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$$

Where CF = contamination factor and n = number of metals.

The different stations of Karamana river show difference in PLI values due to the reasons of location specific nature. The decrease in pollution load with respect to heavy metals noted in some stations is due to the dissolution of metal pollutants. Textural facies observed in the study periods and Pollution Load Index (PLI) worked out in the sediments is depicted in Table 5. The textural data indicate that sediments varying at different stations during premonsoon, monsoon and postmonsoon seasons with a minor change. In general, sand and association of silt/mud in sand are found to be more in the downstream reaches of Karamana river, with a progressive decrease of sand percentage.

In general, the increased values of PLI in the riverine regions compared to coastal regions is attributed to the grain size, clay mineral content and the chemical sink (carbonate fraction, hydroxide fraction and organic fraction) which control the mobility of elements. As stated by Jennes (1976) and Forstner and Wittmann (1983) the redox sensitive Fe and Mn hydroxides and oxides under oxidation conditions, constitute significant sink of heavy metals in aquatic systems. This hydroxide and oxide readily sorb or co-precipitate cations and anions; even a low percentage of Fe (OH)₃ has a controlling influence on the heavy metal distribution in an aquatic system. Seralathan (1987) and Padmalal (1992) have also reported that iron oxide coating is one of the important factors responsible for the concentration of

trace elements in the aquatic environment. The estuarine sediments of the downstream regions of the rivers, due to their finer grain size, contain more clay minerals and organic matter. Consequently, chemical mobile elements are concentrated in fine particles rather than in coarser bed sediments.

5. CONCLUSION

In the upper reaches of the river, the sediments are with high content of pebbles, which transcend to finer grades towards downstream reaches. The marked changes in the flow regimes between downstream and upstream are one of the causative factors responsible for the observed variation in the textural attributes of the riverine sediments. A general increase in the content of fine sediments downstream is observed along with some anomalous behaviours in the dispersal pattern of granulometric fractions at some stations can be explained in terms of the external anthropogenic activities taking place in such areas. The heavy metal distribution in the order of abundance is $Fe > Mn > Zn > Pb > Cr > Cu > Cd$ in Karamana river. Concentration of the heavy metals in the sediments is higher compared to world average concentration of shale samples. This is reflected in relatively higher contamination factor (>1) in sediments of study region which can be attributed to their incorporation by anthropogenic inputs such as agricultural drains, domestic sewage, mining activities and land run-off. The different stations in the river show difference in PLI values due to the reasons of location specific nature. The decrease in pollution load with respect to heavy metals noted in some stations is due to the dissolution of metal pollutants. The estuarine sediments of the downstream regions of the river, due to their finer grain size, contain more clay minerals and organic matter and consequently the chemical mobile elements are concentrated in fine particles rather than in coarser bed sediments.

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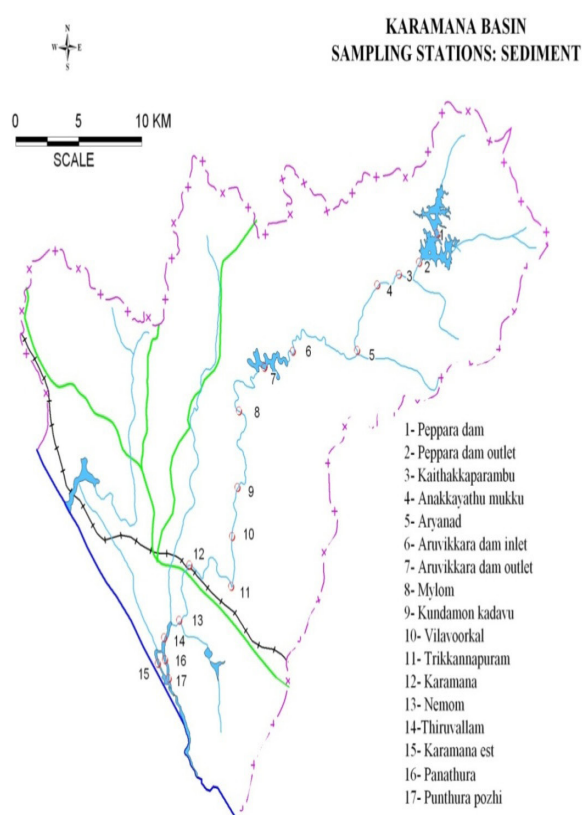


Figure 1: Sediment Sampling Stations

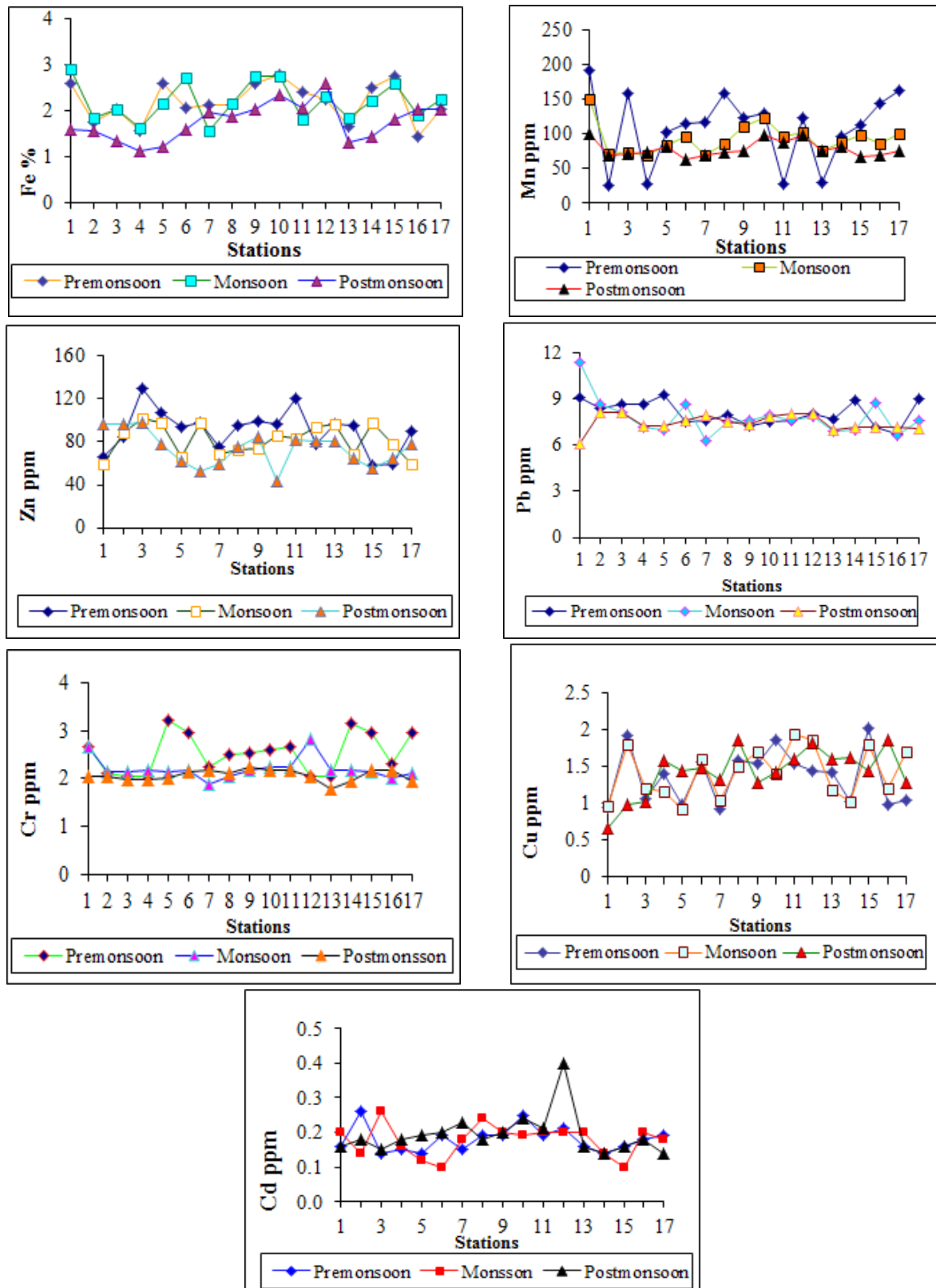


Figure 2: Spatial variation of heavy and trace metals in the bulk sediments of Karamana river.

Table 1: Concentration of various geochemical parameters in bulk sediments of Karamana river (Fe in % and others in ppm), during different seasons**1. Premonsoon Season**

Sample No.	Fe	Mn	Zn	Pb	Cr	Cu	Cd
1	2.60	190.80	66.00	9.10	2.65	0.94	0.16
2	1.73	24.60	84.20	8.41	2.12	1.93	0.26
3	2.03	159.00	129.90	8.71	2.04	1.06	0.14
4	1.56	27.80	106.70	8.67	2.05	1.41	0.15
5	2.60	102.00	93.50	9.28	3.23	0.99	0.14
6	2.04	114.80	98.50	7.50	2.94	1.56	0.19
7	2.13	116.80	75.00	7.63	2.25	0.92	0.15
8	2.12	158.40	95.30	7.98	2.49	1.58	0.19
9	2.59	122.60	98.90	7.26	2.54	1.55	0.19
10	2.78	130.00	96.00	7.54	2.59	1.86	0.25
11	2.40	26.80	120.90	7.62	2.66	1.55	0.19
12	2.24	124.00	77.60	8.04	2.05	1.45	0.21
13	1.66	28.90	97.00	7.68	2.03	1.42	0.16
14	2.50	96.40	95.80	8.92	3.14	1.02	0.14
15	2.76	113.20	57.40	7.16	2.96	2.03	0.16
16	1.44	144.80	59.80	6.77	2.29	0.98	0.18
17	2.01	163.40	89.60	8.99	2.94	1.05	0.19
Average	2.19	108.49	90.71	8.07	2.53	1.37	0.18

2. Monsoon Season

Sample No.	Fe	Mn	Zn	Pb	Cr	Cu	Cd
1	2.89	149.00	60.00	11.40	2.66	0.96	0.20
2	1.85	72.00	88.00	8.66	2.15	1.80	0.14
3	2.01	73.00	102.30	8.15	2.14	1.20	0.26
4	1.62	69.00	98.20	7.14	2.18	1.16	0.16
5	2.14	84.00	66.00	7.02	2.14	0.93	0.12
6	2.70	96.00	98.30	8.67	2.16	1.60	0.10
7	1.56	68.00	69.00	6.32	1.88	1.04	0.18
8	2.14	86.00	73.00	7.51	2.03	1.50	0.24
9	2.73	110.00	73.40	7.58	2.16	1.70	0.20
10	2.74	122.00	86.00	7.98	2.24	1.41	0.19
11	1.80	96.00	83.00	7.63	2.25	1.95	0.20
12	2.30	103.00	94.30	7.89	2.83	1.86	0.20
13	1.82	76.00	96.60	6.94	2.19	1.18	0.20
14	2.22	88.00	69.00	7.03	2.18	1.02	0.14
15	2.60	99.00	98.40	8.77	2.14	1.80	0.10
16	1.89	86.00	78.00	6.62	2.00	1.20	0.20
17	2.24	101.00	60.00	7.59	2.10	1.70	0.18
Average	2.19	92.82	81.97	7.82	2.20	1.41	0.18

3. Postmonsoon Season

Sample No.	Fe	Mn	Zn	Pb	Cr	Cu	Cd
1	1.59	101.00	96.00	6.16	2.04	0.66	0.16
2	1.56	69.00	96.00	8.14	2.03	0.98	0.18
3	1.33	72.00	98.00	8.16	1.98	1.03	0.15
4	1.11	73.00	78.00	7.29	1.99	1.58	0.18
5	1.22	81.00	62.00	7.28	2.02	1.44	0.19
6	1.60	62.00	53.00	7.63	2.14	1.49	0.20
7	1.97	68.00	60.00	7.98	2.16	1.33	0.23
8	1.88	74.00	75.00	7.54	2.12	1.86	0.18
9	2.03	76.00	84.00	7.36	2.23	1.29	0.20
10	2.34	99.00	44.00	7.89	2.16	1.42	0.24
11	2.04	88.00	82.00	8.02	2.18	1.60	0.21
12	2.60	98.00	80.00	8.02	2.05	1.82	0.40
13	1.31	76.00	80.00	6.96	1.80	1.60	0.16
14	1.44	82.00	65.00	7.14	1.96	1.62	0.14
15	1.80	66.00	55.00	7.18	2.19	1.44	0.16
16	2.03	69.00	65.00	7.18	2.16	1.86	0.18
17	2.01	76.00	78.00	7.10	1.96	1.29	0.14
Average	1.76	78.24	73.59	7.47	2.07	1.43	0.19

Table 2: Comparative evaluation of geochemical values in the bulk sediments of Karamana river with that of some rivers of India

Sl. No.	Name of the river	Fe	Mn	Zn	Pb	Cu	Cr	Cd	Reference
1	Karamana river	2.05	93.18	82.09	7.79	2.27	1.4	0.18	Present study
2	Ganges	2.16	400	46	25	21	52	-	Subramanian <i>et al.</i> , (1985)
3	Brahmaputhra	2.9	644	47	13	17	100	-	Subramanian <i>et al.</i> , (1985)
4	Godavari	6.03	1060	53	13	73	126	-	Subramanian <i>et al.</i> , (1985)
5	Krishna	4.23	1040	31	9	49	68	-	Subramanian <i>et al.</i> , (1985)
6	Cauvery	1.76	319	26	10	12	129	-	Subramanian <i>et al.</i> , (1985)
7	Mahanadi	5.61	2020	125	60	57	15	-	Subramanian <i>et al.</i> , (1985)
8	Narmada	3.14	514	50	5	46	-	-	Subramanian <i>et al.</i> , (1985)
9	Tapti	1.09	1300	118	5	126	-	-	Subramanian <i>et al.</i> , (1985)
10	Hemavathy	7.09	204	9	20	4	98	-	Subramanian <i>et al.</i> , (1985)
11	Kabani	17.8	360	17	6	9	180	-	Subramanian <i>et al.</i> , (1985)
12	Bhavani	32.6	535	44	12	12	130	-	Subramanian <i>et al.</i> , (1985)
13	Amaravathi	11.8	184	14	19	3	49	-	Subramanian <i>et al.</i> , (1985)
14	Cauvery basin	12.6	212	13	7	3	54	-	Subramanian <i>et al.</i> , (1985)
15	Bandal	20	3000	-	-	1100	19	-	Singh and Subramanian (1988)
16	Vellar	1.84	3631	117	-	7	252	5	Mohan (1990)
17	Muvattupuzha	5.51	762	65	17	19	107	4	Padmalal (1992)
18	Indian average	2.9	605	16	-	28	87	-	Subramanian <i>et al.</i> , (1985)
19	World's surface rocks	3.59	720	129	-	129	97	-	Ramesh <i>et al.</i> , (1989)
20	World's average soils	4	1000	90	-	90	70	-	Ramesh <i>et al.</i> , (1989)
21	World's average shales	4.6	0.08	85	20	45	7	0.3	Panigrahy <i>et al.</i> , (1997)

Table 3: Correlation matrix of various geochemical parameters in the bulk sediment of Karamana River**1. Premonsoon**

	C-org	Fe	Mn	Zn	Pb	Cr	Cu	Cd
C-org	1.000							
Fe	0.262	1.000						
Mn	-0.098	0.320	1.000					
Zn	-0.231	-0.062	-0.306	1.000				
Pb	-0.679	0.083	0.084	0.257	1.000			
Cr	0.113	0.620	0.244	-0.114	0.210	1.000		
Cu	0.236	0.167	-0.389	0.012	-0.449	-0.081	1.000	
Cd	<u>0.009</u>	-0.011	-0.119	-0.081	-0.293	-0.191	0.639	1.000

2. Monsoon

	C-org	Fe	Mn	Zn	Pb	Cr	Cu	Cd
C-org	1.000							
Fe	0.037	1.000						
Mn	0.036	0.844	1.000					
Zn	0.088	-0.135	-0.352	1.000				
Pb	-0.394	0.651	0.701	-0.011	1.000			
Cr	-0.055	0.424	0.604	0.086	0.578	1.000		
Cu	0.230	0.167	0.115	0.308	0.126	0.171	1.000	
Cd	<u>0.012</u>	-0.176	0.056	-0.068	-0.062	0.112	-0.064	1.000

3. Postmonsoon

	C-org	Fe	Mn	Zn	Pb	Cr	Cu	Cd
C-org	1.000							
Fe	0.519	1.000						
Mn	0.206	0.380	1.000					
Zn	-0.360	-0.226	0.128	1.000				
Pb	0.028	0.313	-0.158	-0.043	1.000			
Cr	0.296	0.561	-0.067	-0.374	0.273	1.000		
Cu	0.609	0.279	-0.121	-0.469	0.179	0.100	1.000	
Cd	0.310	0.666	0.437	-0.123	0.463	0.262	0.341	1.000

Table 4: Concentration and contamination factor of elements in Karamana river.

S l . No:	Element	Concentration Ranges	World Shale Average	Contamination Factor
1	Fe	1.11-2.78%	4.6%	0.31-0.57
2	Zn	44-129.9 ppm	95 ppm	0.71-1.15
3	Pb	6.16-11.4 ppm	20 ppm	0.34-0.44
4	Cu	0.66-2.03 ppm	45 ppm	0.018-0.039
5	Cr	1.8-3.23 ppm	90 ppm	0.022-0.027
6	Cd	0.1-0.4 ppm	0.3 ppm	0.46-0.9

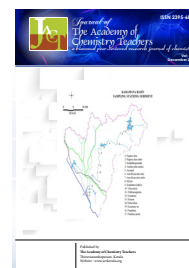
Table 5: Ranges of Texture and Pollution Load Index in Karamana River

Stations	Texture	Pollution Load Index (PLI)
1	Sand	0.1937
2	Sand	0.2063
3	Sand	0.1999
4	Muddy sand	0.1891
5	Muddy sand	0.1885
6	Sand	0.2077
7	Muddy sand to Silty sand	0.1833
8	Muddy sand	0.2112
9	Muddy sand	0.2155
10	Muddy sand	0.222
11	Muddy sand to Silty sand	0.2209
12	Muddy sand	0.2331
13	Sandy clay-Clayey sand Muddy sand	0.1906
14	Sand mud- Muddy Sand	0.1901
15	Sandy mud-Muddy sand	0.2042
16	Sandy silt-Sandy mud-Muddy sand	0.1865
17	Sand	0.1994



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Influence of Coconut Husk Retting on the Ambient levels and Bioaccumulation of Selected Heavy Metals of Paravur Backwaters

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ABSTRACT

One of the major sources of pollution of the kayal's in Kerala, particularly of the interior shallow regions of Paravur kayal, is the phenomenon of retting of coconut husk. The extensive retting activity has made these water bodies into a *foul* smelling, black, dirty, turbid soup of suspended organic debris with practically the whole oxygen dissolved in it replaced with hydrogen sulphide. The retting of coconut husk has resulted in the formation of a curious and complex ecosystem of micro-aerobic and anaerobic properties in the extensive kayal system of Kerala. There is thus severe deterioration of the quality of water in and around the retting zones. The coconut husk retting has also heavily influenced the sediment characteristics. Apart from this the heavy metal distribution in the aquatic system is taken into consideration due to its toxic and harmful effects. In this context it was thought worthwhile to study the accumulation of few heavy metals on the sediments and biotic components of the retting zone and compare the results with similar information collected from a nearby clean area of the Paravur kayal.

Keywords: Coconut husk, retting, heavy metals, sediment, biotic components.

INTRODUCTION

Kerala, the southernmost state of India, is blessed with comparatively extensive estuarine system. These water bodies, are locally known as 'backwaters' or 'kayals'. Unfortunately these water bodies have become highly polluted due to various anthropogenic activities. One of the major sources of pollution of the kayals in Kerala, particularly of the interior shallow regions, is the phenomenon of retting of coconut husk for the production of Coir. Retting of coconut husk have resulted in severe depletion of dissolved oxygen along with the production of H_2S and accumulation of a mixture of several undesired compounds, all which deteriorate the quality of the water^{1,9}. A knowledge on the distribution of heavy metals in the aquatic environment is important in studying the environmental pollution because such elements can be toxic even in traces and cause harmful effects^{5,10}. Many marine organisms are known to

accumulate and concentrate metals. Mangroves may be long term sinks for metals, and deposited metals may be remobilized through plant uptake and exported with plant detritus, increasing the possibility of metals entering coastal food chains.

In this context the present study was aimed at evaluating the contents of some metals in sediments and biotic components of the coconut husk retting zone and non-retting zone of the Paravur kayal.

MATERIALS AND METHODS

The area chosen for the present study was the Paravur Kayal in Kollam district. The Paravur Kayal is a small backwater body situated north of Paravur town. It lies between $8^{\circ} 18'$ and $12^{\circ} 48'$ N lat. and between $74^{\circ} 52'$ and $77^{\circ} 2'$ E long. Two areas of the kayal were selected for the study.

Site 1: Manjadimukku This area is situated 2 km west of the Paravur town. It is a highly polluted site because of the hectic coconut retting activity. This retting zone remains virtually a cesspool of dark, foul smelling, stagnant water for almost the whole year. Both the water and air at and around this part stinks of hydrogen sulphide.

Site 2: Kappil This a very clean area near to the barmouth, was chosen as the non retting zone. Samples for heavy metal assay were collected for both the study areas. Bottom sediments, one selected mangrove plant and one species of fish

were the samples selected for analysis. Sediment samples were collected, using a PVC corer. The mangrove species selected were *Acrostichum aurum* (mangrove fern). *Aplocheilus lineatus* was the fish chosen. Samples were collected from both the study areas at monthly intervals during the premonsoon (Jan –Mar) and postmonsoon (Oct –Dec) periods. All the sample materials were oven dried and grounded using precleaned mortar and pestle. Assay of Fe, Cu, Zn, Pb and Cd in the sediment, mangrove and fish was carried out adopting standard methods ² by Atomic Absorption Spectrophotometry.

RESULTS AND DISCUSSIONS

Table 1

Heavy metal concentrations (mg g⁻¹) in the sediment, fish and mangrove plant from the retting and non-retting zones of the Paravur kayal (Premonsoon period)

Heavy Metals		Study area 1 (Retting Zone)			Study area 2 (Non-retting)			
Jan.		Feb.	Mar.	Mean	Jan.	Feb	Mar	Mean
Sediment	Cadmium	0.011	0.010	0.011	0.011	0.010	0.011	0.011
	Lead	0.026	0.026	0.025	0.026	0.016	0.018	0.033
	Iron	45.540	16.315	26.440	29.432	0.860	5.685	6.145
Fish	Cadmium	0.021	0.175	0.055	0.084	0.028	0.073	0.160
	Lead	ND	ND	0.066	0.022	ND	0.101	ND
	Iron	0.959	0.461	34.547	11.989	2.634	3.119	1.708
Mangrove	Cadmium	0.027	0.021	0.020	0.023	0.021	0.021	0.021
	Lead	0.032	ND	ND	0.011	ND	ND	0.027
	Iron	7.510	2.785	3.600	4.632	1.340	1.046	1.911

Table 2

Heavy metal concentrations (mg g⁻¹) in the sediment, fish and mangrove plant from the retting and non-retting zones of the Paravur kayal (Post monsoon period)

Heavy Metals		Study area 1 (Retting Zone)			Study area 2 (Non-retting)			
Oct.		Nov.	Dec.	Mean	Oct	Nov	Dec	Mean
Sediment	Cadmium	0.025	0.02	0.022	0.022	0.02	0.023	0.03
	Lead	0.06	0.06	0.05	0.056	0.05	0.04	0.052
	Iron	53.5	46.3	46.44	48.74	15.45	15.22	11.12
Fish	Cadmium	0.033	0.035	0.035	0.034	0.045	0.043	0.0460
	Lead	0.06	0.07	0.06	0.063	ND	ND	ND
	Iron	10.59	10.67	10.54	10.60	3.52	3.9	2.8
Mangrove	Cadmium	0.07	0.09	0.07	0.076	0.02	0.03	0.032
	Lead	0.052	0.036	0.033	0.040	ND	ND	ND
	Iron	7.60	7.53	7.500	7.54	2.40	2.06	2.11

ND- Not Detectable

Heavy Metal Contents in Sediment

The concentration of Cd in the sediment of the retting zone was found to be between 0.010 - 0.011 ppm which was similar to that of non-retting zone for the pre monsoon period while in the postmonsoon period retting zone showed a conc. 0.022 ppm, nonretting a conc 0.024 ppm. The present results suggest that the change in the physical and chemical changes caused by coconut husk retting did not have any influence on the Cd load in the sediment. In the retting zone, the mean lead concentration was 0.026 ppm. In the non-retting zone the mean concentration of Pb was 0.022 ppm for the premonsoon period while the retting zone reported a mean conc. of 0.056 ppm in the post monsoon period compared to non retting zone.. The present results are in agreement with these. In Ashtamudi estuary⁴ reported that concentration of Pb in the sediment varied from 0.008 ppm to 0.035 ppm, which is also similar to the present observation. Further, the present results suggest that coconut husk retting does not have any significant effect on the content of Pb in sediments of back water. In the premonsoon retting zone showed a mean iron concentration 29.43 ppm. In the non-retting zone, it was 4.23 ppm, while retting zone in postmonsoon showed a still higher range. The average Fe concentration in the retting zone was more than seven times higher than in the non-retting zone. In comparison, in the Ashtamudi estuary^{4,6,11} have reported Fe concentration in the sediments to range from 1.1 to 3.9 ppm and in the Qilon mangrove sediment^{4,10} reported Fe concentration ranging from 46.91 to 149.45 ppm. The higher concentration of Fe in the sediments of retting zone might be due to the precipitation of Fe as ferric hydroxides. In retting zone there was a foul smell of H₂S due to thiosulphate reduction, which is favoured under anaerobic conditions. Thus the retting zone contains a large amounts of sulphate ions. But sulphate reducing bacteria and iron reducing bacteria are competitors for donors of electrons. By the action of sulphate reducing bacteria on Fe (III) the ferrous sulphide formed is oxidised by acidophilic Fe oxidising bacteria with production of ferric hydroxides and H₂SO₄. This may be the reason for the observed higher

Fe content in the sediment of the retting zone.

Heavy Metal Contents in Fish

The present results also indicate- that retting activity did not have any appreciable influence on the accumulation of these heavy metals by fish. In both the retting and non-retting zones Fe showed an elevated level of concentration in fish, which was significantly higher in fish in the retting zone. In the Ashtamudi estuarine system^{3,7} reported that Villorita cyprinoids had the highest concentration of Fe through out the study. ^{5,6} had reported very high value of Fe content in *Villorita oyprinoides* of Ashtamudi estuary ranging from 6.710 to 13.420 ppm. The present results are in agreement with the earlier studies. The sediments of the retting zone had higher concentration of Fe and it can be expected that the biota in this zone would be have a higher concentration of this metal. It is also noteworthy that majority of animals have a higher requirement of Fe as a conjugant of the respiratory pigment haemoglobin. Therefore, it is likely that animal accumulate more of this element when it is plentiful in the environment. In fish Pb concentrations recorded were 0.066 ppm and 0.101 ppm dry weight in retting and non-retting zone, respectively. The concentration of Pb in the tissues of fishes in Ashtamudi estuary ranged between 0.005 and 0.066 ppm^(3,4). reported a concentration of Pb upto 0.050 ppm from Caribbean waters indicating that such levels are indeed possible. The mean Cd concentration in fish from the retting zone in premonsoon was 0.083 ppm. In fish from the non-retting zone the mean Cd concentration was 0.087 ppm. For postmonsoon retting showed a mean value of 0.034 and non-retting 0.044 ppm. In this case in both the zones Cd residue in fish was comparatively low and it did not vary much between the two zone.

Heavy Metal Contents in Mangrove

Both in the retting and non-retting zones, cadmium concentrations in mangrove were almost the same in the premonsoon but in postmonsoon conc. varied with retting showing a mean value 0.07 and non retting 0.027 ppm. As in the case of Pb residue in fish, in mangrove also Pb was detected only in one month in both retting and non-retting zones.

The values recorded were 0.032 and 0.027 ppm, respectively. High values of Pb have been reported in mangrove from the retting zone the mean concentration of Fe was 4.631ppm. In the non-retting zone, average Fe concentration was 1.432ppm. High concentration was noted in non retting zone in the postmonsoon period. Many mangrove species are reported to contain very high concentrations of heavy metals such as Fe and Mn. The toxic effects of these metals get reduced due to the action of chelating substances present in these plants. According to^{5, 6, 8} the value of Fe recorded in the mangrove species *Sonneratia alba* in Goa mangroves was 8.112ppm. The species *Avicennia officinalis* has been reported to contain 0.281 to 6.344ppm dry wt. of Fe.

Conclusion

The results on the assay of heavy metal concentration in the sediment, fish and mangrove from the retting and non-retting regions of Paravur kayal show that, the concentrations of Cd and Pb in all three components were negligible and were not markedly different between the two regions and the concentrations of Fe in all three components assayed were high and differed significantly between the retting and non-retting regions, its concentrations being much higher in all three compartments in the retting zone than those in the non-retting zone.

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I **Dr. Manohar D. Mullassery**, Asst. Professor of Chemistry, FMN College, Kollam, do hereby declare that the particular given above are true to the best of my belief.

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