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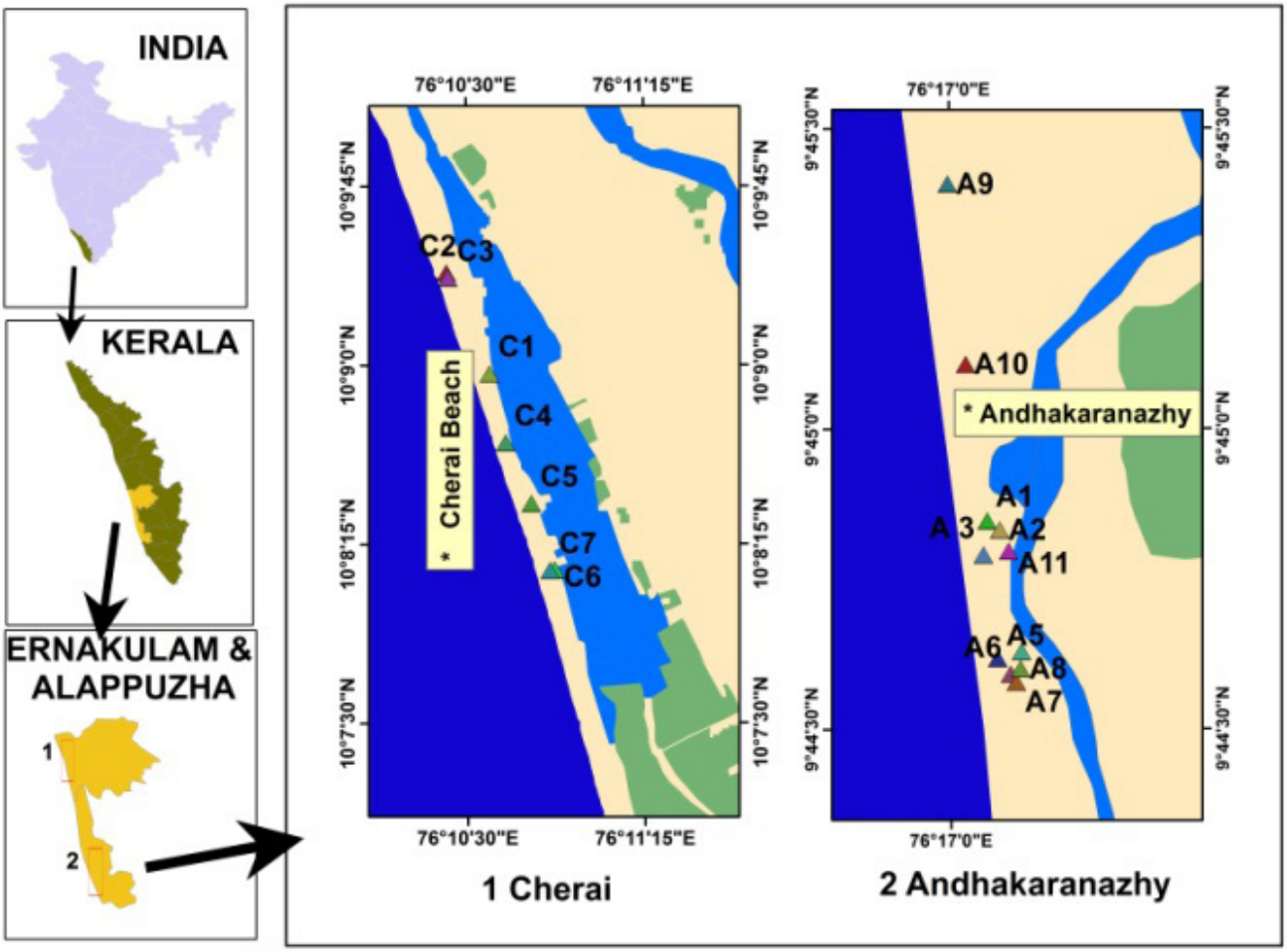

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Dynamic mechanical, Swelling and Oil resistance studies of Montmorillonite clay in grouping with TiO_2 on Natural rubber latex films

Vijayalekshmi.V *and Chithra PG

Department of Chemistry, S.N College for Women, Kollam, Kerala - 691001

*Author for correspondence:

E-mail: lekshmi500@gmail.com

Abstract

Nanocomposites of Natural rubber latex (NRL), nanoclay (MMT-Na^+) and Titanium dioxide (TiO_2) were prepared using solution mixing method. The structural properties were studied using X-ray diffraction (XRD) Scanning electron microscopy (SEM) Transmission electron microscopy (TEM) and thermogravimetric analysis. XRD and TEM results indicated that an exfoliated structure was formed by the addition of small amount of filler. Swelling and UV- Visible Properties was done. Dynamic mechanical analysis was also studied.

Keywords: Natural rubber, TiO_2, Montmorillonite, nanocomposites

Introduction

Polymeric materials have been used for a wide range of industrial applications in packaging and protective coatings [1]. The use of clay filled Natural rubber latex as components of composites for packaging materials is very popular because of the better resistance to solvents, increased thermal stability, improved Dynamic mechanical properties etc. The nanoclay has high barrier property and high aspect ratio [2,3].Titanium dioxide (TiO_2) is used for enhancing the UV absorption property.

Objectives

- UV Absorbing devices
- Shielding and semiconducting materials
- Low permeating materials
- Anti-static coatings

Experimental

Aqueous dispersion (2%) of layered clay was prepared by an ultrasonic stirrer. The compounding ingredients and TiO_2 nanoparticles with an average particle size of 15nm were added with nanoclay in different proportions into the Natural rubber latex. The mixture is then properly stirred for 2 hours at room temperature by solution mixing method.

Results and Discussion

1.XRD

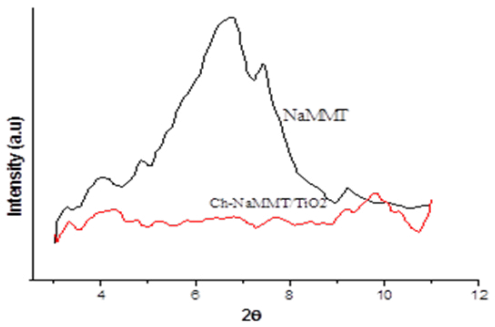

Fig .1 XRD of NRL & NRL- NaMMT/ TiO_2 0.8 nanocomposites

For Cloisite Na^+ the 2θ is 7.2^0 and its d -spacing is 12.26 Å. For NRL- NaMMT/TiO_2 nanocomposite, 2θ shift to a lower value 4.3^0, d spacing has increased to 20.5 Å. The XRD result shows the formation of an exfoliated nanocomposite with increase in d-spacing.

2. SEM and TEM Images

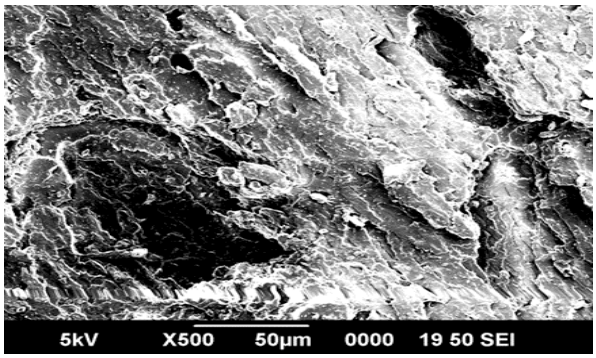

Fig 2a SEM of NRL Nanocomposite

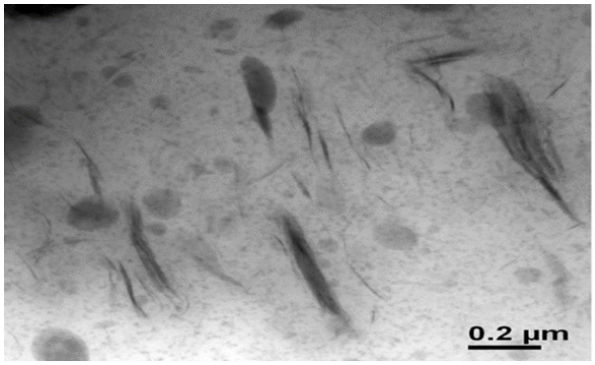

Fig 2b TEM of NRL nanocomposite

Particles are well dispersed into the Natural rubber latex from SEM and partial intercalation and exfoliation is observed from TEM images.

3. Swelling Properties

a) Chemical resistance

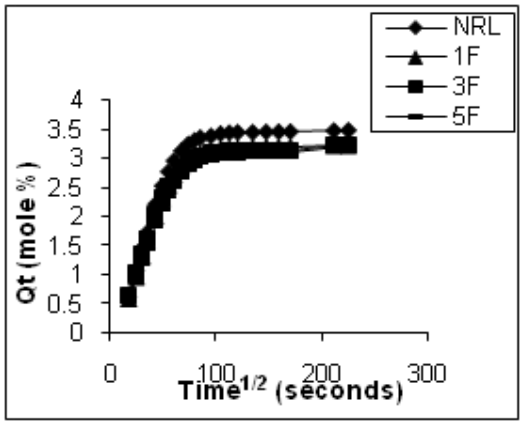

Fig 3a. Sorption curves of the NRL vulcanizates at 303K in Toluene

This is due to the reduced availability of space for solvent molecules in the intercalated structure of the nanocomposites. This also shows the strong interaction between the filler and the matrix, which limits the toluene diffusivity within the entangled polymer matrix.

b) Oil Resistance

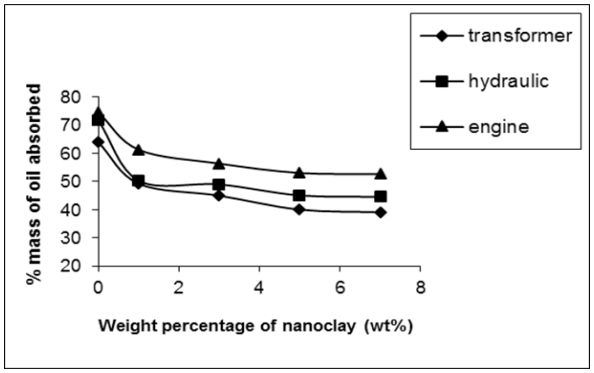

Fig.3b Oil resistance of NRL-MMT/TiO_2 in 3 different oils

The oil resistance was studied in 3 different oils namely transformer, engine and hydraulic. The rate of swelling decreases by the increase in filler loading. Transformer oil shows better swelling resistance.

4. Dynamic mechanical properties

In dynamic mechanical analysis, the frequency is proposed to be varied from 1 to 50Hz under frequency sweep mode at a rate of 2 Hz/min and temperature of 60^0C. The elastomer chains are intercalated in the layered silicate structure resulting in change in modulus and damping behavior which is due to the contact surface area of the filler. Storage modulus increases with increase in clay loading. A 400 % increase in storage modulus is observed for 5wt% clay filled system.

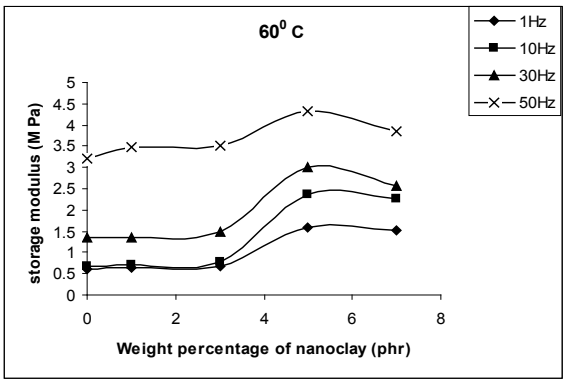

Fig 4a. Storage modulus vs nanoclay curves of NRL nanocomposites

Loss modulus shows a decreasing trend with filler loading upto 5 wt% and then shows an increasing trend. Loss modulus decreased by 11.09% by the addition 5wt% nanofiller which

indicates lower heat dissipation factor at 30 Hz. At 50Hz the loss modulus intensifies due to higher friction of particles.

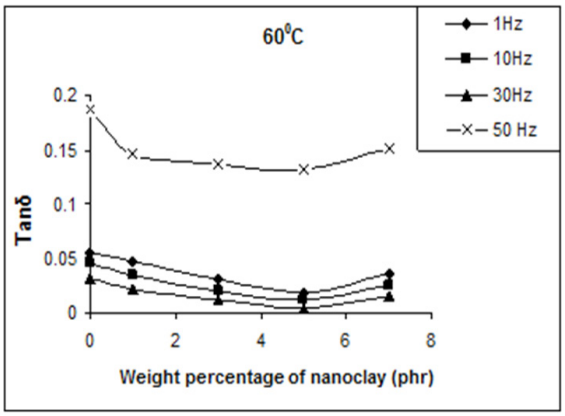

Fig 4b Tanδ vs nanoclay curves of NRL nanocomposites

Tan δ shows a damping performance of the nanocomposites. Concentration of layered silicates shows a reduction in the heat dissipation factor or loss tangent due to the restricted mobility of the chains.

5. UV-Visible analysis

From UV spectrum, the wavelength of NRL and nanocomposites are found to be 339 nm and 363nm respectively. From this it is clear that the absorption is maximum for the MMT/ TiO_2 filled sample. From Tauc's plot the band gap of NRL and its NRL nanocomposites is found to be 2.1 eV and 2.7 eV. This shows that the semi conducting property has increased for nanocomposites.

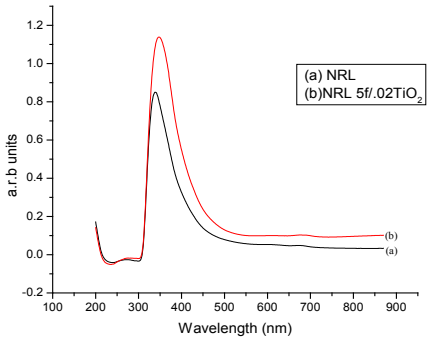

Fig 5. shows the UV absorption spectrum of NRL and NRL nanocomposites

Conclusion

The 2θ value and d-spacing of nanocomposites decreased by 2.9^0 and increased by 7.74 Å respectively. From the SEM images, it is observed that particles are unvaryingly dispersed, which means a better interaction between the filler and the matrix. A partially intercalated and exfoliated structure is observed from TEM images. This result reveals the better interaction of NRL in the MMT structure. The swelling properties shows a better result. Storage modulus increases while loss modulus and tan δ decrease with increase in the frequency, in frequency sweep method at 5 wt% filler loading. From Tauc's plot the band gap has increased from 2.1 eV to 2.7eV.

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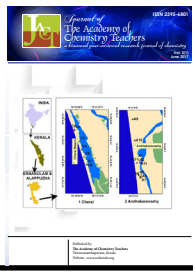


Synthesis, Characterisation, and Fluorescence study of some Benzothiazole derivatives

Sarau Devi A[1] and Reena Ravindran[2]*

1. Department of Chemistry, Fatima Mata National College, Kollam, Kerala - 691001

2. Department of Chemistry, Sree Narayana College, Chempazhanthy, Thiruvananthapuram, Kerala - 695587

*Author for correspondence:

E-mail: reena1234@gmail.com

Abstract:

Three new benzothiazole derivatives namely 2-(4-methoxyphenyl) benzothiazole, (mpb), 2-(3-methoxy-4-hydroxyphenyl)benzothiazole, (mhpb), 2-(2-hydroxyphenyl) benzothiazole, (hpbH) have been synthesised in ethanolic medium. The prepared compounds were characterized by elemental analysis FTIR, electronic spectroscopy. The fluorescence properties of all the compounds were explored and found that all are fluorescent with mhpb exhibiting intense fluorescence property.

Keywords: benzothiazoles, spectral studies, fluorescence.

1. Introduction

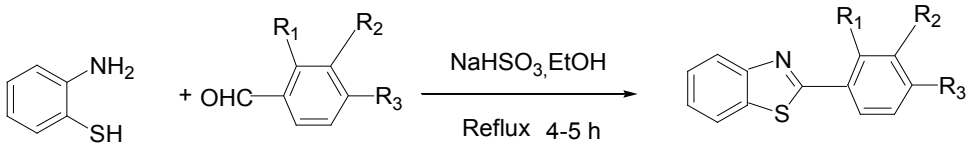
Benzothiazoles are biologically active heterocyclics with luminescence property, formed by the fusion of benzene ring and thiazole ring. The presence of thiazole subunit in the large delocalized π-electron system enhance the hyperpolarizability of benzothiazoles and are good candidates for the display of large non-linear responses, hence properly substituted benzothiazoles are excellent NLO chromophores[1,2]. Substituted 2-phenylbenzothiazoles are of great interest now, due to their pharmacological and optical activities that include antitumor, antifungal, antioxidant and photosensitizing properties[3-6]. Benzothiazole can coordinate through nitrogen or sulfur atoms on either side of the heterocyclic ring depending on the nature of metal ion[7]. Benzothiazole derivatives, which function as multidentate ligands can form complexes that are stabilized by non-covalent interactions leading to supramolecular architectures. Most of these complexes are assumed to exhibit enhanced biological activities and interesting material properties. Based on these objectives we synthesized the following substituted 2-phenyl benzothiazole derivatives. In this paper we describe the synthesis and spectral characterisation of a group of substituted 2- phenyl benzothiazole derivatives. The fluorescence properties are also reported here.

2. Materials and Method

High purity o-aminothiophenol, anisaldelyde, salicyladelyde, vanillin and sodium bisulphite, were purchased from Merck and used as received for preparing benzothiazole derivatives. Ethanol was dried over fused $CaCl_2$ and distilled. Other solvents were purified and dried by using standard procedure.

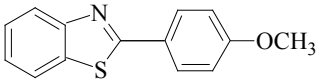
2.1. Synthesis of benzothiazole derivatives (mpb, mhpb and hpbH)

Synthesis of compounds mpb, mhpb and hpbH were carried out by adopting a reported procedure[8] (Scheme 1). Equimolar mixture of $NaHSO_3$ (1.25g, 0.012M) and corresponding aldehyde, viz. anisaldehyde (1.63g, 0.012M) for mpb, vanillin (1.82g, 0.012M) for mhpb, and salicylaldehyde (1.47g, 0.012M) for hpbH, were refluxed in ethanol (15mL) for 15-20 minutes. To the mixture o-aminothiophenol

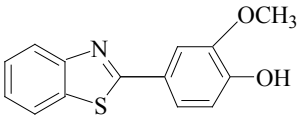


R1= H, R2 = H, R3 = OCH3 for mpb
R1= H, R2 = OCH3, R3 = OH for mhpb
R1= OH, R2 = H, R3 = H for hpbH

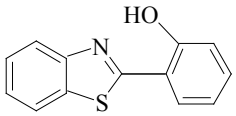
Scheme 1: Synthesis of substituted 2- phenyl benzothiazoles



2-(4-methoxyphenyl)benzothiazole, mpb



2-(3-methoxy-4-hydroxyphenyl)benzothiazole, mhpb



2-(2-hydroxyphenyl)benzothiazole, hpbH

Figure 1: Structures of substituted 2-phenylbenzothiazoles: mpb, mhpb, hpbH

Table 1: Physical and analytical data of benzothiazole derivatives

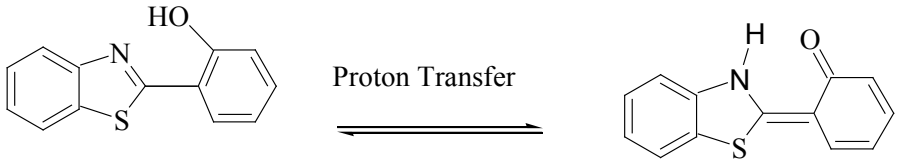
Compound	Color	Found (calc.)%			
		C	H	N	S
mpb ($C_{14}H_{11}NOS$)	Colorless	69.51(69.68)	4.75(4.59)	5.63(5.80)	13.42(13.28)
mhpb ($C_{14}H_{11}NO_2S$)	Colorless	65.42(65.34)	4.21(4.30)	5.62(5.44)	12.63(12.46)
hpbH ($C_{13}H_9NOS$)	Colorless	68.75(68.69)	3.79(3.99)	6.32(6.16)	14.28(14.10)

(1.25g, 0.01M) was added and continued to reflux for 4-5 h. On slow cooling, colourless crystalline compound formed in each case was filtered, washed with water, recrystallized from ethanol and dried over fused $CaCl_2$. M.p. of mpb, 110 °C; mhpb, 171 °C; hpbH, 129 °C. The chemical structures of substituted 2-phenyl benzothiazoles, mpb, mhpb and hpbH are given in figure 1.

3. Results and discussion

The physical and analytical data of the three benzothiazole derivatives are listed in Table 1. The elemental analysis data obtained are in good agreement with stoichiometries of 2-(4-methoxyphenyl)benzothiazole, mpb; 2-(3-methoxy-4-hydroxyphenyl)benzothiazole, mhpb and 2-(2-hydroxyphenyl)benzothiazole, hpbH.

The structure of hpbH exhibits keto-enol tautomerism due to an ultra-fast excited-state intramolecular proton transfer (ESIPT). The phenolic –OH group (enol form) in the ground state forms an intramolecular hydrogen bond with the nearby ring N atom of benzothiazole moiety in non-polar solvent. Since the intramolecular hydrogen bonding force is strong, it drives skeletal motion from a non-planar enol structure to a planar keto structure (Figure 2). However, when a protic or polar solvent is utilized, the solvation effect increases the intermolecular hydrogen bonding with the polarity of the solvent thereby decreasing the intramolecular hydrogen bonding. Therefore, the ESIPT from enol to keto is depressed and an enol form predominates[9,10].



Enol tautomer

Keto tautomer

Figure 2: Tautomerism in hpbH

3.1. Infrared spectra

The IR spectra of the compounds mpb, mhpb and hpbH are shown in Figures 3 to 5. The important peaks are assigned in Table 2. The appearance of bands in the 1625-1300 cm^{-1} range is due to overall ring skeletal (benzene and thiazole ring) stretching mode[11,12]. The characteristic ν(C=N) vibrations of thiazole moiety for mpb, mhpb and hpbH are assigned at 1597 cm^{-1}, 1592 cm^{-1} and 1588 cm^{-1} respectively and ν(C-S) band at 687 cm^{-1}, 716 cm^{-1} and 700 cm^{-1} respectively[13]. Bands in the region 1308-962 cm^{-1} correspond to the CH- in plane deformation of benzene and thiazole ring while out of plane deformation are observed in the range of 860 – 716 cm^{-1} [14]. The ν(O-H) of mhpb appeared as a broad band in the region 3200-2800 cm^{-1} while ν(O-H) of hpbH appeared as a weak peak at 3057 cm^{-1}. The phenolic C-O stretch for mhpb is observed at 1191 cm^{-1} and the same for hpbH is at 1219 cm^{-1}. The O-CH_3 stretching mode for mpb and mhpb is ascribed to the peaks at 1021 cm^{-1} and 1007 cm^{-1} while bending mode to the peaks at 434 cm^{-1} and 438 cm^{-1} respectively[15].

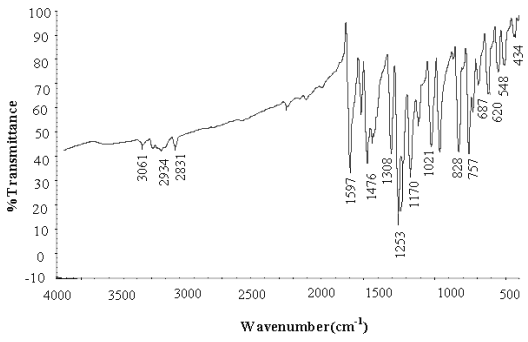


Figure 3: IR spectrum of mpb

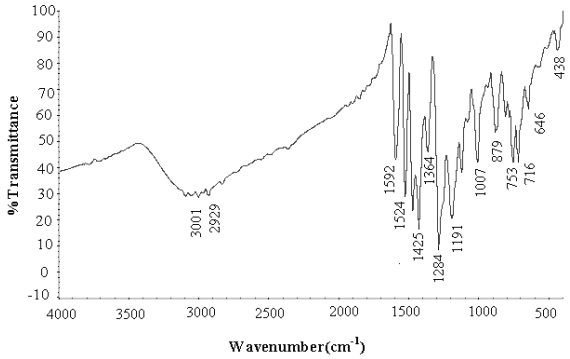


Figure 4: IR spectrum of mpb

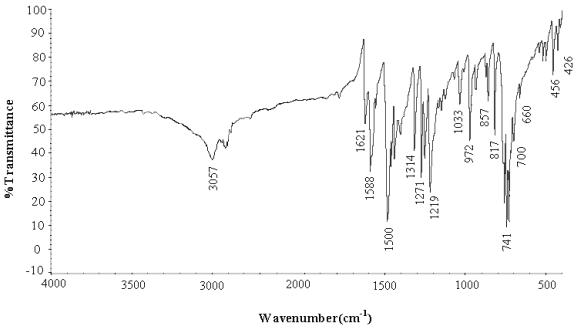


Figure 5: IR spectrum of hpb

3.2. Electronic spectra.

Figure 6 shows the electronic spectra of mpb, mhpb and hpbH in the methanolic solution (10^{-3} M). Important bands observed are listed in table 3. The position of absorption bands is influenced by the structure of the compounds and it is in good agreement with values reported in literature [16]. The compound mpb, has a methoxy group in para position of substituted phenyl moiety of benzothiazole. Hence the spectrum of mpb shows two high intensity bands of almost same absorption

Table 2: IR spectral assignments (cm^{-1}) of the compounds mpb, mhpb, hpbH

compound	ν(O-H)	ν(C=N)	ν(CS)	ν(C-O)	ν(OCH_3)
mpb	-	1597	687	-	1021, 434
mhpb	2800-3200	1592	716	1191	1007, 438
hpbH	3057	1588	700	1219	-

Table 3: Electronic spectral assignments (nm) of the compounds mpb, mhpb, hpbH

Compound	Absorbance λ_{max} (nm)
mpb	212, 310
mhpb	220, 285, 328
hpbH	214, 286, 330

maxima, at 212 nm due to π-π* transitions of benzo chromophore and at 310 nm due to π-π* transitions of substituted phenyl ring[17,18]. The n- π* transitions of benzothiazole ring is buried under more intense π-π* transitions at 310 nm[19]. In compounds mhpb and hpbH, the bands due to π-π* transitions of benzo chromophore are observed at 220 nm and 214 nm respectively. The band displayed at 285 nm and 286 nm respectively in mhpb and hpbH are assigned to π-π* transition of substituted phenyl ring. The long wavelength (> 300 nm) band observed at 328 nm and 329 nm has been attributed to n-π* transitions of thiazole ring and OH chromophore of mhpb and hpbH respectively[20-22]. Thus, three significant absorption bands are observed for mhpb and hpbH compounds and two for mpb. The magnitude of absorption band intensities increases with increase in resonance effect of substituted groups. Therefore mhpb exhibit higher intensity bands than the others[23].

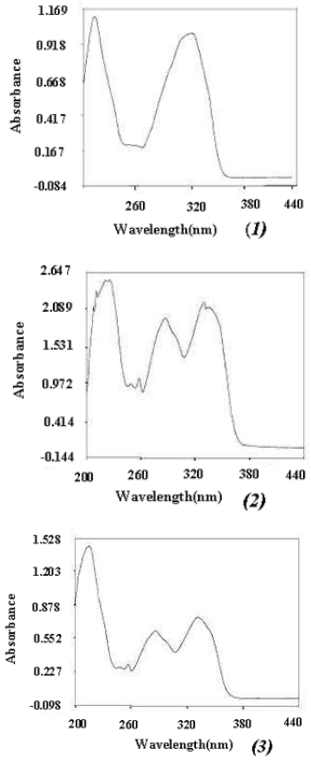


Figure 6: Electronic spectra of mpb (***1***), mhpb (***2***) and hpbH (***3***)

3.3 Fluorescent Properties

The fluorescence spectrum of the compounds mpb and mhpb are shown in Figure 7. The spectrum of hpbH under different excitation conditions are given in Figures 8. It has been proved that benzothiazoles exhibit strong luminescence in solution and in solid state, due to the presence of electron-withdrawing heteroaromatic ring incorporating with the π conjugated system and electron donating chromophores[24,25]. The emission spectrum of mpb measured in methanolic solution at 298K, is characterized by a broad band centered at 378 nm, upon excitation at 310 nm. The emission spectrum of mhpb under the same excitation condition gives emission peak at 408 nm, upon excitation at 285 nm. Eventhough all the compounds have good fluorescence quantum yield, mhpb exhibit about 10-fold enhanced fluorescence than mpb in solution at room temperature due to the presence of additional –OH chromophore which impart stabilization to intermediate transition state[26].

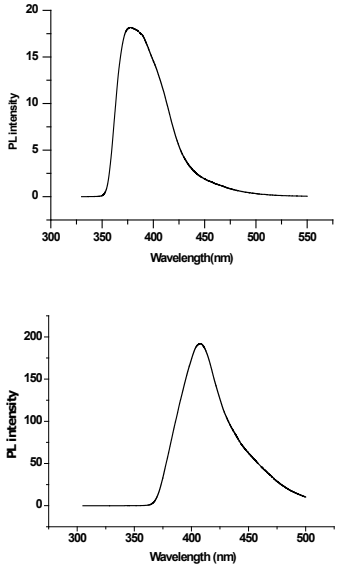
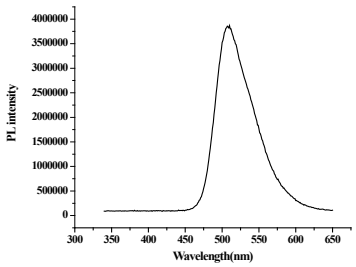


Figure 7: Fluorescence spectrum of mpb and mhpb in methanol



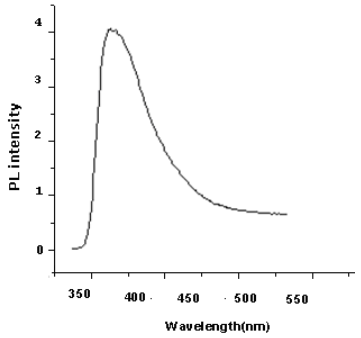


Figure 8: Solid state and solution state(methanol) fluorescence spectrum of hpbH

In solution, depending on the nature of solvent, the emission spectra of hpbH include two emission peaks due to the formation of two tautomeric forms produced by excited-state intramolecular proton transfer (ESIPT) effect[27]. In polar solvent, where hydrogen bonding forces strongly predominate, enol tautomeric form gives emission peak at ~386 nm. In non-polar solvent strong intramolecular hydrogen bonding drives skeletal motion from a nonplanar enol structure to a planar keto structure giving emission peak at ~512 nm [9,28]. The ESIPT molecules are normally more stable as enol form in the ground state and as keto forms in the excited state[21]. Here for hpbH, in solid state at room temperature, only fluorescence from the excited keto species is observed at ~ 510 nm. The peak at 387 nm in methanolic solution is attributed to the emission of enol isomer [9,29]. A bathochromic shift in the peaks of mhpb and hpbH are explained on the basis of electron donating ability of –OH chromophore and solvent effect. The spectral changes are influenced by electron donating or withdrawing effect of substituents, a bathochromic shift for electron donating and hypsochromic shift for electron withdrawing substituents[18].

Conclusion

A set of three phenyl benzothiazole derivatives, *viz* 2-(4-methoxyphenyl) benzothiazole, mpb; 2-(3-methoxy-4-hydroxyphenyl)benzothiazole, mhpb and 2-(2-hydroxyphenyl) benzothiazole, hpbH were prepared and characterized by elemental analyses, infrared, electronic and spectral studies. The fluorescence properties of all these compounds were explored. The compound mhpb exhibits intense fluorescence property compared to the other two derivatives due to the presence of additional –OH chromophore which impart stabilization to intermediate transition state.

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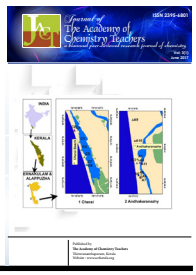

Corrosion Indices, Drinking and Irrigation Water quality of Andhakaranazhy and Cherai Coastal Regions of Kerala

V. Sivanandan Achari*, P. Deepa, M. S .Ambili and T. Regi George

School of Environmental Studies, Cochin University of Science and Technology, Kochi, Kerala- 682022

*Author for correspondence:

E-mail: vsachari@gmail.com

Abstract

Andhakaranazhy (09° 44' 50N, 76° 17' 07E) and Cherai (10.14227°N 76.178255°E) are two coastal sections of Kerala had severely affected by Tsunami waves on 26 December 2004. Scarcity of fresh ground water is a major problem in these areas, because of salt water intrusion and other anthropogenic activities such as tourism and sand mining. The study discussed in this paper comprises of the determination suitability of ground water for industrial and irrigation purposes.

Introduction

Coastal areas have a variety of complex environments like estuaries, bays, beaches. There is an equilibrium existing between the fresh water aquifer and brackish water. So the excess withdrawal of fresh water may result the intrusion of sea water into the land. Many of the coastal ground water aquifers of Kerala are suffering from sea water intrusion and intensified over the years due to over exploitation. Only few dependable fresh ground water sources are available to meet their needs. Urban development causes direct and indirect effect on the ground water quality in coastal aquifers [1]. Ground water chemistry plays an important role in the assessment of ground water quality. In one of the post-tsunami study found that the surface and well waters in the tsunami affected areas were contaminated by seawater and maintained brackish in nature [2]. Laluraj have studied the ground water chemistry of shallow aquifers in the coastal zones of Cochin ,found that ground water present in the shallow aquifers of the some of the stations were poor in quality and beyond the potable limit as per WHO & ISI[3]. Post tsunamic study of ground water quality in Kerala coast found that its quality was deteriorated due to the tsunami impact. Assessment of ground water quality variation along the tsunami affected coast of Kerala has been a major research work and many reports are known with respect to pre and post tsunamic situation[4,5,6,7 & 8].

Materials and Methods

Study areas are Andhakaranazhy (09^0 44' 50N, 76^0 17 07E) in Alappuzha district and Cherai (10.14227°N 76.178255°E) in Ernakulam district. Andhakaranazhy coast (09° 44' 50N, 76° 17' 07E) of Alappuzha is a barrier islet section having the impact of continuous action of scrolling waves, where the back waters merge into the sea through a seasonal sand bar mouth. Two barges operated by large mechanized shutters are there in the tidal canals near north and south end of confluence. These shutters are flow regulators of saline water to prevent and protect the neighboring paddy fields which are connected to the back waters. During monsoon, water is released into the sea by lifting these shutters; hence prevent flooding in the location. Cherai coast (10.14227°N 76.178255°E) is known as the golden beach of Kerala. This beach is rightly considered as one of the most beautiful beaches in Kerala. It is a beautiful combination of sea and backwaters

surrounded by coconut trees and paddy fields. Due to proximity to sea and saline inundation, fresh water is a scarce resource though the region is a tourist destination. Eighteen (18) ground water sources were selected from both of the study areas Andhakaranazhy (9 dug wells and 2 bore wells) and Cherai (1 bore well and 6 dug wells). Sampling and further analysis of prominent water quality parameters were done for a period of twelve months from January 2012 to December 2012, following the standard protocols [9].

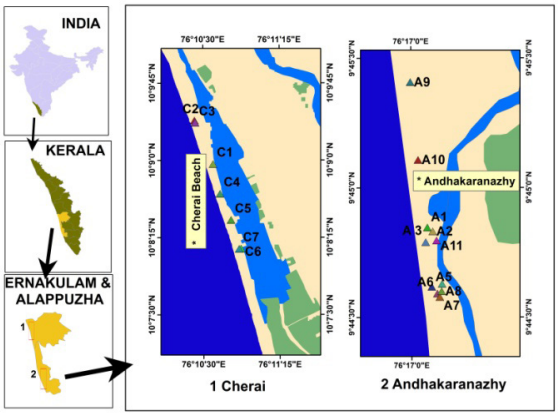

Figure 1: Location Map of the Study areas

Table 1: Physico-chemical parameters of ground water quality of Andhakaranazhy and cherai during the year 2012

Water Quality Parameter	Annual Mean of Ground Water Samples		WHO (Desirable Limit)	BIS (Desirable Limit)
	Andhakaranazhy	Cherai		
pH	7.6±0.25	7.3 ± 0.38	6.5-8.5	6.5-8.5
EC(mS/cm)	0.8±0.62	2.4 ± 5.11		
TA(mg/L)	330.2±117.23	152.3 ± 87.49		200
DO(mg/L)	3.6±1.99	3.0 ± 2.77		
BOD(mg/L)	13.5±6.92	21.4 ± 11.93		
TH(mg/L)	290.0±108.93	433.1 ± 653.53	150	300
Ca^{2+}(mg/L)	83.2± 26.46	85.6 ± 114.53	75	75
Mg^{2+}(mg/L)	18.5±11.39	53 ± 105.03	30	30
TDS(mg/L)	576.3±398.92	1603 ± 3355.41		500
Na^{+}(mg/L)	119.2±96.21	229.4 ± 358.59	200	
K^{+}(mg/L)	8.3± 8.98	16.5 ± 30.73		
Cl^{-}(mg/L)	161.6±169.9	570.8 ± 1049.69	250	250
SO_4^{2-}(mg/L)	10.2±14.91	25.9 ± 36.88	500	200
NO_3^{-}(mg/L)	1.3± 1.41	2.8 ± 2.49	50	45
PO_4^{-}(mg/L)	0.2± 0.18	0.4 ± 0.4		
Total Iron(mg/L)	0.8± 0.84	1.2 ± 1.22	0.3	0.3

Results and Discussions

The annual mean of physico-chemical parameters of 18 ground water sources of Andhakaranazhy and Cherai coasts during the year 2012 shown in Table.1.Parameters like total alkalinity, total dissolved solids, total iron and calcium ions of Andhakaranazhy region exceed the BIS, WHO standards. In Cherai total dissolved solids, total hardness, calcium, magnesium, sodium, chloride and total iron were exceeding these limits. It may be due to the salt water intrusion in to the ground water aquifer.

Irrigation Suitability

Salinity indices such as Sodium Percent (Na %), Sodium Adsorption Ratio(SAR) and Kelly's index(KI)are important parameters for determining the suitability of ground water for agricultural use. Table 2 shows the irrigation water quality parameters of Andhakaranazhy and Cherai coast. SAR, Na% and KI of Andhakaranazhy coast shows that the water is within the limits and suitable for irrigation purposes. But in Cherai some of the ground water sources were exceeding the standard limits of irrigation water quality parameters, may be due to the salt water intrusion.

Table2. Irrigation Water Quality Parameters of ground water sources of Andhakaranazhy and Cherai coasts of Kerala

Parameter	Range	Class	No of samples	
			Andhakaranazhy	Cherai
SAR (Richards, 1954)	0-10	Excellent	11	6
	10-18	Good		1
	18-26	Fair		
	>26	Poor		
Na % (Wilcox,1955)	< 20	Excellent		
	20-40	Good	5	1
	40-60	Permissible	5	5
	60-80	Doubtful	1	1
	>80	Unsuitable		
KI (Sundary, 2009)	<1	Suitable	8	3
	>1	Unsuitable	3	4

Industrial Suitability

Many indices were used to predict the industrial suitability of ground water such as Langelier Saturation Index (LSI), Ryznar Stability Index (RSI) and Aggressiveness Index (AI). Table 3 shows the stability indices of the ground water of the study area. LSI and AI of Andhakaranazhy coast shows a scale forming (non –corrossive) behavior of water in all (11) ground water sources. But RSI of nine (9) ground water sources shows values between 6.2-6.8. So the water is considered as neutral .The remaining two sources in the range of 6.8-8.5, the water is slightly aggressive. In Cherai LSI of all (7) the ground water sources characterizing a corrosive behavior. RSI and AI showed a corrosiveness behavior in most of the water samples. This corrosive nature of the water may be due to the increased amount of dissolved solids due to sea intrusion [10,11 &12].

Table 3: Indices of Corrosion of ground water sources of Andhakaranazhy and Cherai coasts of Kerala

Parameter	Range	Significance	No of samples	
			Andhakaranazhy	Cherai
LSI	LSI < 0	Corrosive		7
	LSI = 0	Neutral		
	LSI > 0	Scale forming	11	
AI	AI ≤10.0	Highly aggressive		
	AI 10.0-11.9	Moderately aggressive		6
	AI ≥12	Non-aggressive	11	1
RSI	RSI < 5.5	Heavy scale likely to form		
	5.5 < RSI < 6.2	Moderate scale formation likely		
	6.2 < RSI < 6.8	Water is considered neutral	9	
	6.8 < RSI < 8.5	Water is aggressive and corrosion is likely	2	5
	RSI > 8.5	Water is considered very aggressive, and substantial corrosion is possible		2

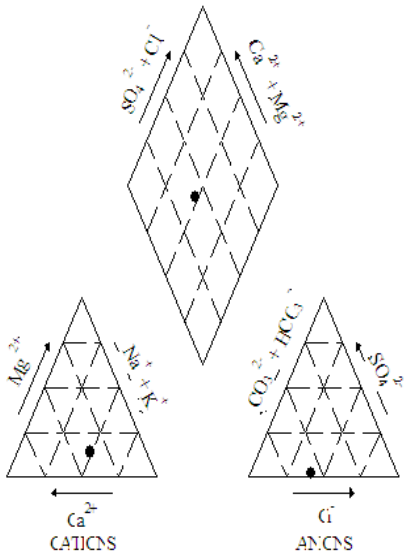

Figure 2: Piper diagram of Andhakaranazhy coast during the year 2012

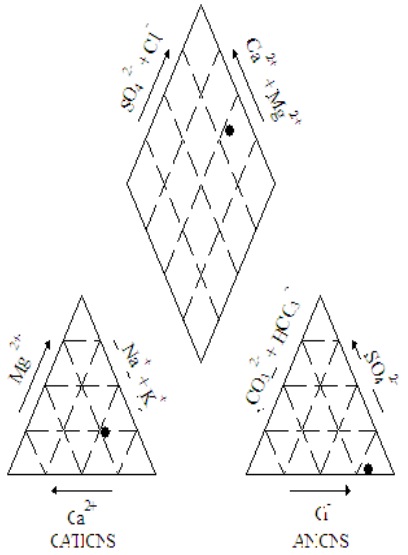

Figure 3: Piper diagram of Cherai coast during the year 2012

Piper Diagrams

Piper diagram is a graphical representation of the water quality data can be used as an interpretation tool. It consists of two triangles; one for cations and one for anions and these two are interlocked by a diamond. Concentrations are expressed in milli equivalent per litre. It provide very valuable knowledge on the water type, precipitation or solution behaviour, mixing character and ion exchange phenomena [13]. Figure 2 & 3 shows piper diagrams of Andhakaranazhy and Cherai coast of Kerala respectively. The diagram showed a temporary hardness behavior along the Andhakaranazhy coast. There is no dominating cation and bicarbonate is the anion type. The hydro chemical facies is characterized by Ca^{2+}- Mg^{2+}- HCO_3^- prominent water. But in Cherai coast, the water is saline type with sodium dominating cationic triangle and the anion is chloride. So the hydrochemical facies is NaCl type.

Conclusions

Many factors such as pH, temperature, total dissolved solids, alkalinity and hardness are affecting the ground water quality of the study area. Dissolved chemical constituents in ground water may cause the corrosion or scale formation behavior. It may be due to the salt water intrusion into the ground water aquifer. Bicarbonate of calcium and magnesium ions are responsible for the temporary hardness behavior of the ground water. The reason behind the increased amount of bicarbonate ion in ground water is sulphate reduction mechanism. The saline nature of the ground water is mainly attributed by the increased concentration of sodium and chloride ions in ground water aquifer as a result of sea water intrusion.

Acknowledgement

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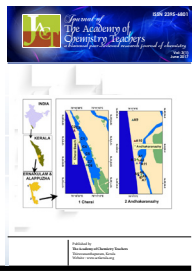


Photophysical Properties of Perylenediimide Derivatives

Sabah Sajeeb[1], P. Rajagopal[2] and P. Manoj[1*]

1. Department of Chemistry, St. Michael's College, Cherthala, Mayithara P O, Alappuzha, Kerala - 688539
2. Department of Physics, C. M. S. College, Kottayam, Kerala - 686001

*Author for correspondence:

E-mail: pmanoj2k@gmail.com

Abstract

We report the photophysical properties of perylene diimides (PDI) derivatives namely perylenediimide-flurene derivative [PDI-FLU] and perylenediimide-phenyl derivative [PDI-PHE]. The photophysical properties were investigated using absorption and fluorescence spectroscopic techniques. The UV-Vis absorption spectrum of PDI-FLU is characterized with a peak at 327, 454 and 561 nm in solution state. In the case of PDI-PHE the absorption spectra is characterized with peaks at 319, 495 and 530 nm in solution and 244 and 495 nm in thin film. The emission spectrum of PDI-FLU and PDI-PHE is characterized with a peak centered on 664 and 582 nm respectively. From the optical spectral data we calculated various spectral parameters such as Stoke's shift, optical band gap and full width at half maximum (FWHM). The band gap of the PDI derivatives was found to be 1.81 eV for PDI-FLU and 1.77 eV for PDI-PHE.

Keywords: Perylene diimides, Organic Electronics, Photophysics, Bulk heterojunction Solar Cells.

Introduction

The need for production energy from easily available and renewable source was the reason that made scientist to utilize light for electricity. Inorganic photovoltaic cells based on silicon was thus discovered, even though this invention was useful for solving energy crises, expensive production cost of silicon based solar cells became major issues for its vast utilisation. As the demand for low cost energy production increased, scientists started to experiment on organic-polymer based elements for manufacturing photovoltaic cells, which was found to be the cheapest and easiest way of producing clean energy from light.[1]

Quantum theory of light is the basic principle behind all types of photovoltaics. Frequency or colour of the light is the factors that affect the energy of a photon, which is a discrete packet of energy of electromagnetic waves. To excite electrons across forbidden gap from valence band to the conduction band in the case of semiconductors the energy of photons from visible spectrum is sufficient. By absorbing photon, electrons will get excited and after few nanoseconds it will come back to the ground state. In the case of photovoltaics in addition to the usual phenomenon, there is a built in asymmetry which pulls the electron and hole into an external circuit before they recombine in the ground state and this is common to all type of photovoltaics. This mechanism results in the collection of electrons and positively charged holes to get collected at the electrode which is used to generate electric potential to do work.

Photovoltaics are generally characterized on the basis of three factors the short circuit current (J_{SC}), the open-circuit voltage (V_{OC}), and the fill factor (ff). The fill factor can be defined as the ratio between the maximum power delivered to

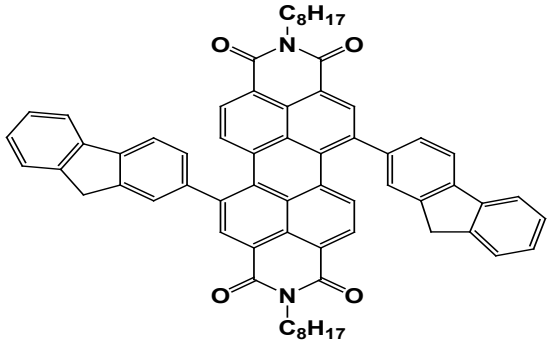
an external circuit and the potential power or it is a function of charge migration to electrode.[2] At zero bias, the short circuit current is the product of the number of photons absorbed and the efficiency of free charge carrier generation and collection. Theoretically, open-circuit voltage relates to the difference between the highest occupied molecular orbital of the electron donor and the lowest unoccupied molecular orbital of the electron acceptor.[3] The solar cell based on organic materials is a potential alternative to inorganic solar cells because of its low cost, large area fabrication, flexibility and environmental friendly devices.[4] But the efficiency of organic solar cell is low which limits its commercial applications. Therefore, scientists across the globe are putting tremendous efforts to push the efficiencies of organic solar cells to a value that is competent with the inorganic counterparts.

One of the major reasons for the low power conversion efficiency (PCE) in organic solar cell is the narrow absorption of organic materials. In general, organic materials have large band gap, therefore, only a small amount of the incident photon is absorbed by the sample. In order to improve the efficiencies of organic photovoltaic devices (OPVs) different approaches such as synthesizing new donor and acceptor molecules, optimizing the band gap of the polymers to enhance the short circuit current and increasing the open circuit voltage have been applied.

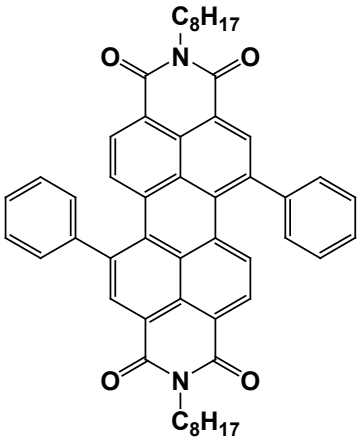
Poly(3-hexylthiophene) (P3HT) is the most studied donor polymer and its qualities include good solubility in organic solvents, moderately high field effect hole mobility and tendency to form ordered domains.[5] From the literature it can be understood that extensive investigations of the p-type semiconductors have been performed.[6] However, the development of n-type material still lags because of the deficiency of the high performance material. Generally n-type semiconductors are air sensitive molecules and electrons are easily trapped. The device life time and performance have been limited because of the instability of the material. A common n-type material used in bulk heterojunction solar cell is [6,6]phenyl-C61 butyric acid methyl ester (PCBM)[7], which has poor stability and shelf life. Therefore, researchers are trying to find out an alternative to PCBM which provides more opportunities including enhanced stability and efficiency. In this context perylenediimides (PDIs) offer a better choice.[8] Perylene systems are resistant to photo degradation, relatively easy to manipulate synthetically and have tunable energy levels. The BHJ solar cells with PDI as acceptors have low efficiencies and it can be improved by tuning the molecular architecture of perylene.[9] Optical and electrical properties, similar molar extinction with n-type semiconductors, electron mobility and thermal stability of perylenediimides (PDIs) paved way for its application in laser dyes, organic solar cells, optical switches, organic field effect transistors, logic gates, photosensitizers, sensors, biological applications, light harvesting arrays, and artificial photosynthetic systems.[10-14] PDIs are used in various dimensions because of its important electron accepting and electron donating properties and its unusual photocurrent amplification properties made these compounds potential for solar cell fabrication. In this context we propose to investigate the photophysical properties of two PDI derivatives namely perylenediimide-flurene derivative [PDI-FLU] and perylenediimide-phenyl derivative [PDI-PHE].

Experimental Section

The derivative of perylenediimides PDI-PHE and PDI-FLU used for this study is a gift from Dr. Ganapathi Balaji. Dichlorobenzene is used as solvent for the analysis. The chemical structure of PDI-PHE and PDI-FLU is shown in figure 1.



PDI-FLU



PDI-PHE

Figure 1. Chemical structure of PDI-PHE and PDI-FLU

Preparation of Thin Film

Spin coating technique is used for the preparation of thin films. In spin coater, a small amount of the fluid resin is placed at the centre of the substrate and it is spinned at high speed. PDI-FLU and PDI-PHE are individually made soluble in dichlorobenzene and both of them are made into a thin film by coating it on a cleaned glass substrate. Spin coating was done using five programs in which the acceleration is done two times, the first acceleration with a spin speed of 1900 rpm for 10 seconds and second acceleration with a spin speed of 1990 rpm for 20 seconds. Thin film thus produced is used for the optical studies.

Optical Spectra

The absorption spectra of the samples were recorded using the Shimadzu UV-2600 spectrophotometer. The spectral range of the spectrophotometer is adjusted to 200-900 nm. Dichlorobenzene is used as solvent for solution phase absorption spectra for both the compounds. The emission spectra were recorded by using Shimadzu RF-5301 spectroflurometer.

Results and Discussion

Absorption and Emission Spectroscopy

The optical absorption spectra of PDI-FLU and PDI-PHE in solution are shown in figure 2. It is observed that the solution state spectra of both PDI-FLU and PDI-PHE are characterized with multiple peaks. In the case of PDI-FLU, absorption maximum is observed at 561 nm with a shoulder peak at 454 nm and another sharp peak at 327 nm. For PDI-PHE the absorption maxima is observed at 530 nm with a shoulder peak at 495 nm and a sharp peak at 319 nm.

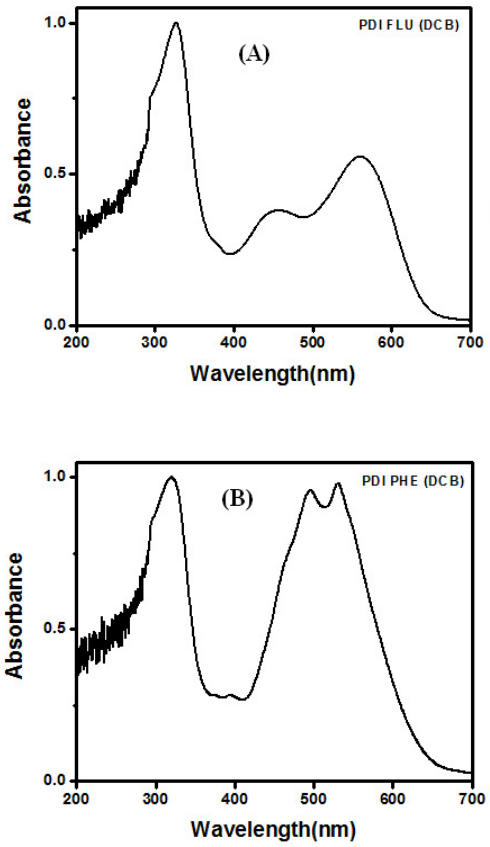
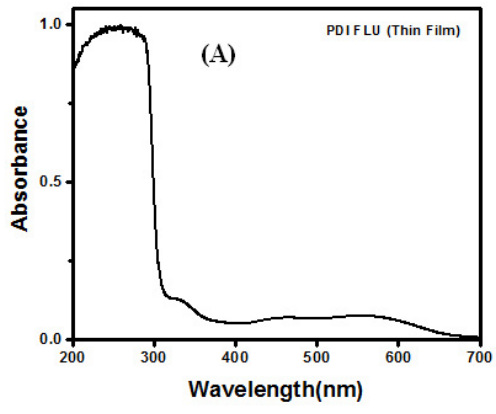


Figure 2. Optical absorption spectra of (A) PDI-FLU and (B) PDI-PHE in the liquid state

The absorption spectra of PDI-FLU and PHI-PHE in thin film are shown in figure 3. It is observed that the thin film spectra of PDI-FLU are characterized with a broad absorption centered at 555 nm and a peak at 259 nm. In the case of PDI-PHE the absorption maxima is observed at 495 nm and 244 nm.



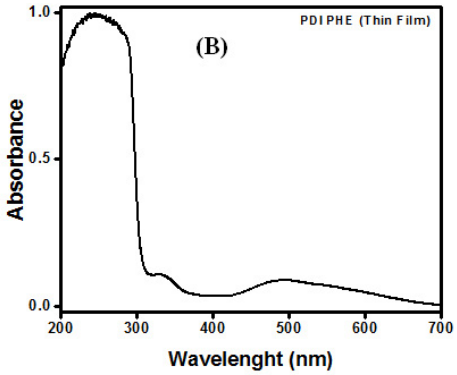
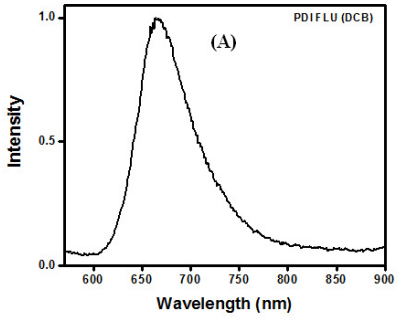


Figure 3. Absorption Spectra of (a) PDI-FLU and (b) PDI-PHE in thin film

Solution state fluorescence spectra of the samples were recorded in dichlorobenzene by using the excitation wavelength corresponding to the absorption maximum. The emission spectra of PDI-FLU and PDI-PHE in solution state are shown in figure 4. The spectrum is characterized with a sharp peak at 664 nm for PDI-FLU and at 582 nm for PDI-PHE.



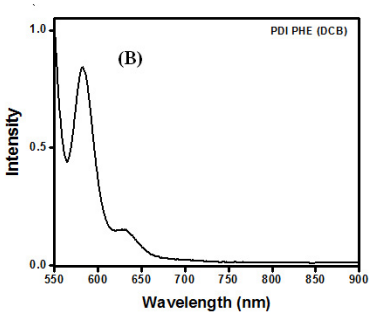


Figure 4. Emission spectra of (A) PDI-FLU and (B) PDI-PHE in liquid state.

The optical properties of these molecules is summarized in table 1.

From the data it is found that there is variation in absorption maximum for PDI-FLU and PDI-PHE in the solution state and in thin film. For PDI-FLU, the difference between the absorption maxima (Δλ) is found to be 6 nm and for PDI-PHE it is found to be 35 nm. Stoke's shift was also calculated from the absorption and emission spectra of PDI-FLU and PDI-PHE. The Stoke's shift for PDI-FLU is found to be 103 nm and for PDI-PHE is 52 nm. That is, stokes shift of PDI-FLU is almost twice as that of PDI-PHE. Full width at half maximum (FWHM) were calculated for both the compounds from absorption and emission spectral data. In the case of absorption spectra in solution state FWHM is found to be 73 nm and 83 nm and in thin film it is found to be 100 nm and 99 nm for PDI-FLU and PDI-PHE respectively. In solution state emission spectra FWHM for PDI-FLU is 67 nm and 27 nm for PDI-PHE. The band gap of these molecule was calculated from the solution state absorption spectra by

Table 1. Optical properties of PDI-FLU and PDI-PHE

Sample	Absorption (nm)		Δλ	Emission (nm)
	Solution	Thin Film		Solution
PDI-FLU	327, 454, 561	259, 555	6 nm	664
PDI-PHE	319, 495, 530	244, 495	35 nm	582

Sample	Stokes Shift	Optical Band Gap (eV)	FWHM		
			Absorption		Emission
			Liquid	Film	
PDI-FLU	103 nm	1.81	73 nm	100nm	67 nm
PDI-PHE	52 nm	1.77	83 nm	99 nm	27 nm

using an equation, Bandgap (eV) = 1240/Cutoff wavelength (nm). In the case of PDI FLU the band gap was found to be 1.81 eV and for PDI PHE it is about 1.77 eV.

Conclusion

In conclusion, we studied the optical properties of the two perylene derivatives, namely PDI FLU and PHI PHE.The optical absorption spectra of PDI-FLU is characterized with a peak at 327, 454 and 561 nm in solution state and 259 and 555 nm in thin film. In the case of PDI PHE the absorption spectra is characterized with 319, 495 and 530 nm in solution and 244 and 495 nm in thin film. It is noteworthy that both these oligomers have a broad absorption, which is one of the key factors for the fabrication of high performance organic photovoltaic devices. The band gap of the PDI derivatives was found to be 1.81 eV for PDI-FLU and 1.77 eV for PDI-PHE. From these observations it can be concluded that these molecules may be a potential candidate for the fabrication of organic photovoltaic devices. But the optimization of surface morphology of thin film and charge transport property is to be investigated. Therefore, a future study in this direction is currently under progress in our laboratory.

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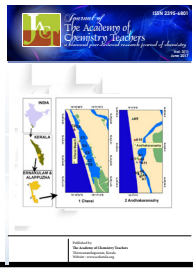


A review on the phytochemistry of *Piper cubeba* & bioactivities of the marker compound cubebin and its semi-synthetic derivatives

Dhanya S. R* and Mangalam S. Nair

Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, Kerala - 695019

*Author for correspondence:

E-mail: dhanyasethulekshmi@gmail.com

Abstract

Plants have been the major source of drugs and drug leads since antiquity. *Piper cubeba*, commonly known as tailed pepper, is an important medicinal plant belonging to Piperaceae family. Berries of the plant find extensive application in various traditional systems of medicine and have been reported to be a rich source of bioactive lignans and neolignans. The lignan lactol, cubebin is the major compound isolated from the berries of *P. cubeba*. The present review highlights the phytochemistry and pharmacology of *P. cubeba* as well as describes the bioactivities of cubebin and its synthetic derivatives.

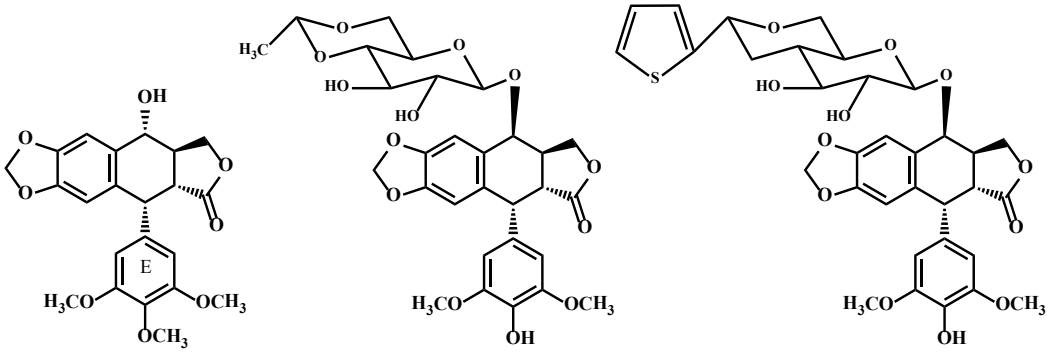
Keywords: *Piper cubeba*, lignans, neolignans, cubebin, hinokinin, cubebin derivatives

1. Introduction

All over the world, since time immemorial, Natural products (NPs) obtained from plants have been the basis of medicinal preparations used for the treatment of various diseases. Pure bioactive compounds isolated from plants have played a significant role in modern drug discovery process, especially in the development of anticancer and antihypertensive therapeutic agents.[1,2,3] A revival of interest in natural drugs has started in last decade mainly because of the wide spread belief that NPs are less toxic than than synthetic drugs.[4] Also, isolation of compounds from medicinal plants attracted the attention of scientific community much earlier than from marine organisms since the later is not commonly employed in traditional systems of medicine.[5]

Lignans are an important class of plant secondary metabolites which have attracted much attention in recent years due to their ubiquitous occurrence in a variety of plant species as well as due to their fascinating pharmacological and biological activities such as anticancer, antiviral, anti-inflammatory, antioxidant and hepatoprotective activities.[6] Among the various lignans present in nature, the lignan lactone - podophyllotoxin (**1**) is the one which has gained maximum attention in recent years due to its anticancer activity. Etoposide (**2**) and teneposide (**3**), which are semi-synthetic derivatives of podophyllotoxin are currently in clinical use for the treatment of various forms of cancers such as small-cell lung cancer, testicular cancer, leukemias and lymphomas.[7]

Plants belonging to Piperaceae family especially those belonging to the *Piper* species are rich sources of bioactive lignans and neolignans and have attained worldwide attention due to their enormous medicinal, economical as well as commercial importance.[8] *Piper cubeba*, an important medicinal plant belonging to this



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species contains a large number of bioactive lignans in it.[9] The plant is commonly known as 'Tailed pepper' in English, 'Kannkolam' in Sanskrit and 'Valmulaku' in Malayalam. It is a perennial woody climber, native to Indonesia and cultivated in the southern region of India. Fruits of the plant are globular with a slender stalk attached to its base and are hence known as 'tailed pepper'. The dried berries of the plant are used in traditional systems of medicine for the treatment of inflammation, helminthiasis, wounds, ulcers, cough, rheumatism, hay fever etc.[10] Famous Indian *Ayurveda* physicians Charaka and Sushruta prescribed the paste of *P. cubeba* fruits as mouth wash. Dried fruits are also used for the treatment of dental diseases, fever, cough etc.[11] Seeds of the plant are utilized in the preparation of many Ayurvedic formulations like 'dasamoolarishta', 'angoorasava', 'jirakadyarishta', 'bala thaila' etc.[12] In *Unani* system of medicine it is used for the treatment of renal diseases and recent studies have shown that the powdered berries show nephroprotective activity.[13]

2. Phytochemistry and pharmacology of *P. cubeba*

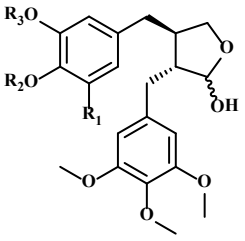
The essential oil obtained from *P. cubeba* seeds contains monoterpene hydrocarbons including sabinene, α-thujene, α-pinene *p*-cymene, etc., as well as sesquiterpenes like caryophyllene, copaene, α and β-cubebene, cubebol, δ-cadinene etc.[14] Essential oil of *P. cubeba* berries have been reported to have activity against the parasites *Schistosoma mansoni* (causative agent of schistosomiasis),[15] *Trypanosoma cruzi* (causative agent of Chagas disease) and *Leishmania amazonensis* (causative agent of leishmaniasis)[16]. Of these, leishmaniasis is a major problem in certain states of India. Essential oil and oleoresins of *P. cubeba* have been reported to show antimicrobial as well as antioxidant activities.[14b] It also showed activity against *Streptococcus faecalis, Bacillus pumilus* and *Pseudomonas solanacearum*.[17]

Ethanol extract of *P. cubeba* seeds have been reported to possess anti-inflammatory[18] and hepatoprotective[19] activities. Alcoholic extract showed cytotoxic activity against various breast cancer cell lines (MCF-7, MDA-MB-468, MDA-MB-231)[20] and androgen-dependent prostate cancer growth.[21] *P. cubeba* extracts also showed activity against *Streptococcus salivarius*, *Streptococcus mitis, Enterococcus feacalis,*[22] promastigotes of *Leishmania donovani*[23] and hepatitis C virus.[24]

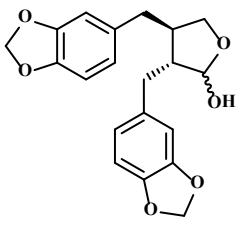
Phytochemical investigation of *P. cubeba* seeds have been carried out by several groups and it has been found that the berry of the plant is a rich source of bioactive lignans and neolignans.[9] . Lignans and neolignans isolated from the berries of the plant are listed in table **1**. Apart from lignans, two oxygenated cyclohexanes viz., piperenol C (**28**) and (+)-piperenol triacetate (**29**)[25] as well as two sesquiterpenes viz., (5α,8α)-2-oxo-1(10), 3,7(11)-guaiatrien-12,8-olide (**30**) and (1α,2β,5α,8α,10α)-1,10-epoxy-2-hydroxy-3,7(11)-guaiadien-12,8-olide (**31**)[26] were also reported from the plant. Other compounds such as α–asarone (**32**), 2,4,5-trimethoxyphenylacetone (**33**), 1-(2,4,5-trimethoxyphenyl)-1,2-propanedione (**34**), asaronaldehyde etc. were also reported from the plant. Structures of the lignans and neolignans are given in fig. **1** and structures of other compounds isolated from *P. cubeba* are given in fig. **2**.

Table 1: Lignans isolated from the berries of *Piper cubeba*

Name of the compound	Compound No	Reference
Clusin	**4**	27
Cubebin	**5**	
Cubebinin	**6**	
Cubebininolide	**7**	28
Cubebinone	**8**	
Dihydroclusin	**9**	27
Dihyrocubebin	**10**	
α-O-ethylcubebin	**11**	29
β-O-ethylcubebin	**12**	
Hemiariensin	**13**	
Heterotropan	**14**	29
Hinokinin	**15**	27
4-hydroxycubebinone	**16**	26
Isoyatein	**17**	28
Kadsurin A	**18**	25
Magnosalin	**19**	29
Medioresinol	**20**	26
5-methoxyclusin	**21**	
5'-methoxyhinokinin	**22**	29
α-methylcubebin	**23**	26
2-(3'',4''-methylenedioxy-benzyl)-3-(3',4'-dimethoxybenzyl) butyrolactone	**24**	28
Piperenone	**25**	25
Thujaplicatin Trimethylether	**26**	28
Yatein	**27**	



4; R_1 = H, R_2+R_3 = CH_2
6; R_1 = OCH_3, R_2 = R_3 = CH_3
21; R_1 = OCH_3, R_2+R_3 = CH_2



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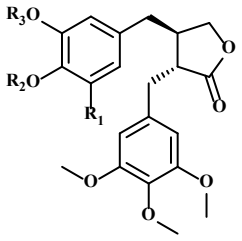
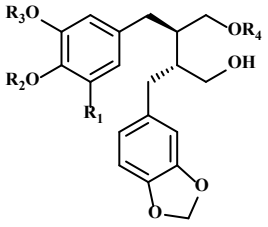
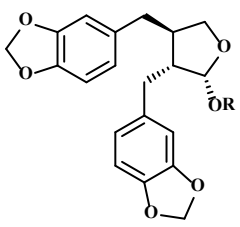


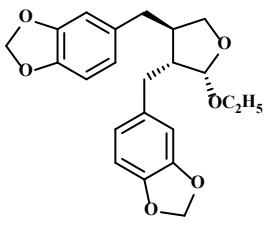
7; R_1 = OCH_3, R_2 = R_3 = CH_3
8; R_1 = OCH_3, R_2+R_3 = CH_2
26; R_1 = H, R_2 = R_3 = CH_3
27; R_1 = H, R_2+R_3 = CH_2



9; R_1 = OCH_3, R_2 = R_3 = CH_3 R_4 = H
10; R_1 = H, R_2+R_3 = CH_2 R_4 = H
13; R_1 = H, R_2+R_3 = CH_2 R_4 = Ac



11; R = C_2H_5
23; R = CH_3



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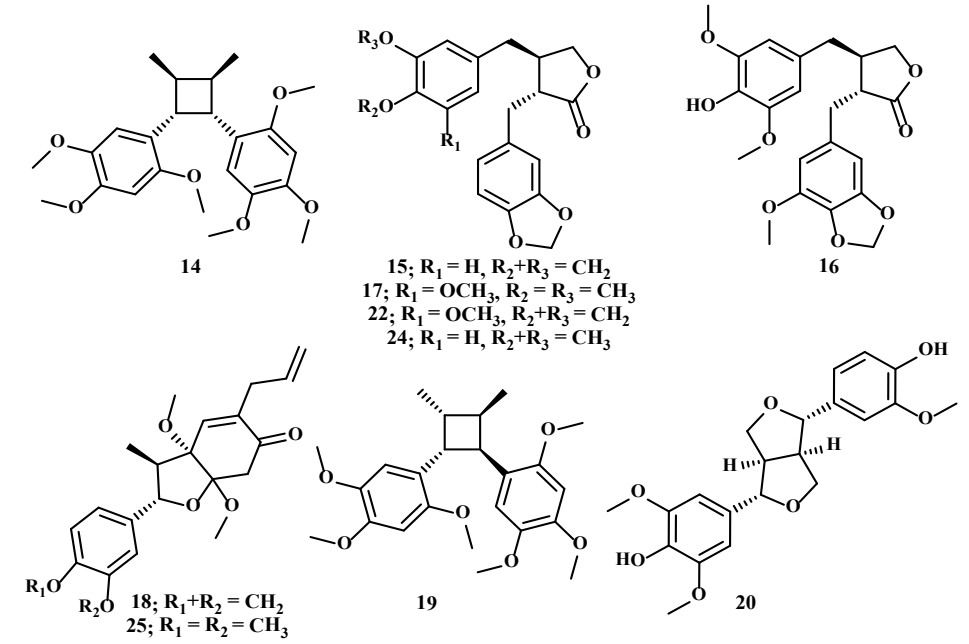


Figure 1: Structures of lignans and neolignans isolated from *Piper cubeba*

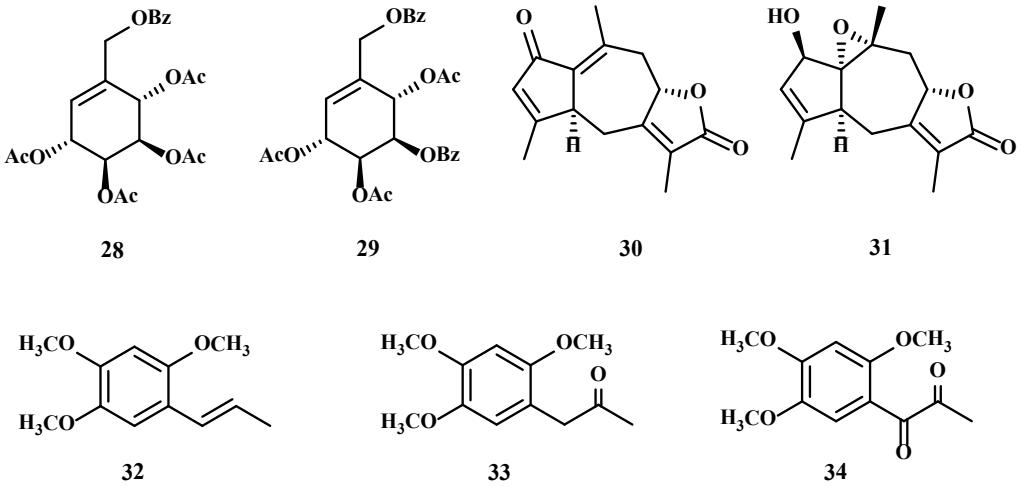


Figure 2: Structures of other compounds isolated from *Piper cubeba*

3. Bioactivities of the marker compound cubebin and its semi-synthetic derivatives

The major compound present in *P. cubeba* seeds is the butyrolactol lignan, (-)-cubebin.[9,27] (-)-Cubebin has been reported to have trypanocidal,[30] anti-inflammatory,[31] analgesic,[32] vasorelaxant,[33] antimycobacterial and antiprotozoal[34] activities. Even though (-)-cubebin is the most abundant compound in *P. cubeba,* there are only limited reports available on its synthetic derivatives and their bioactivity studies. In 2005 da Silva *et al.*[35] reported the synthesis of cubebin derivatives such as (-)–hinokinin, (-)-6,6'-dinitrohinokinin and (-)-6,6'-diaminohinokinin by employing straight forward synthetic procedures. Antiinflammatory and analgesic activities of the compounds were evaluated and the synthesised compounds showed better activity than cubebin. In the same year Silva *et al.* reported the synthesis of (-)-*O*-acetyl cubebin, (-)-*O*-benzyl cubebin, (-)-*O*-(*N,N*-dimethylaminoethyl)-cubebin, (-)-hinokinin and (-)-6,6'-dinitrohinokinin (fig. **3**). These compounds were evaluated for their activity against *Trypanosoma cruzi*, the asogic agent of Chagas disease. Hinokinin was found to be the most active compound where as (-)-*O*-benzyl cubebin and (-)-*O*-(*N,N*-dimethylaminoethyl)-cubebin showed moderate activities.[36] Use of cubebin for the treatment of erectile dysfunction has been patented in the year 2011 by Albuquerque *et. al.*[37]

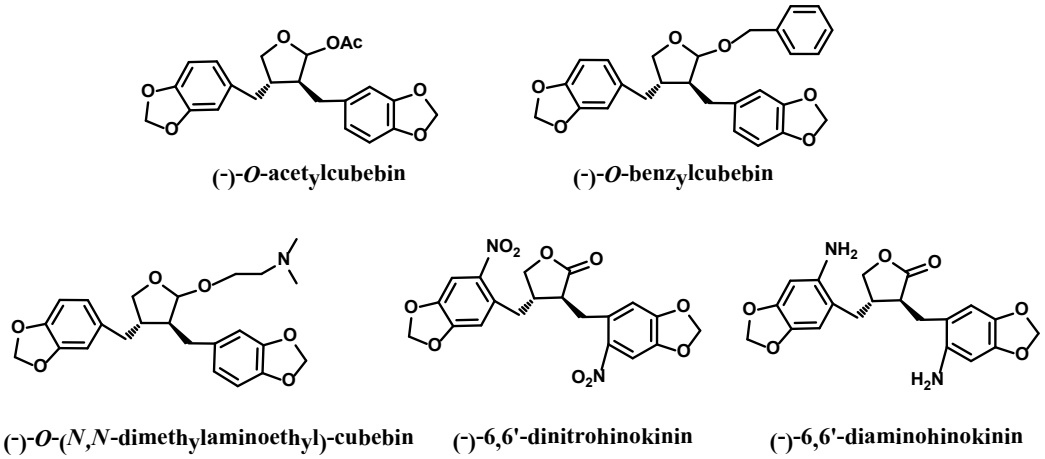
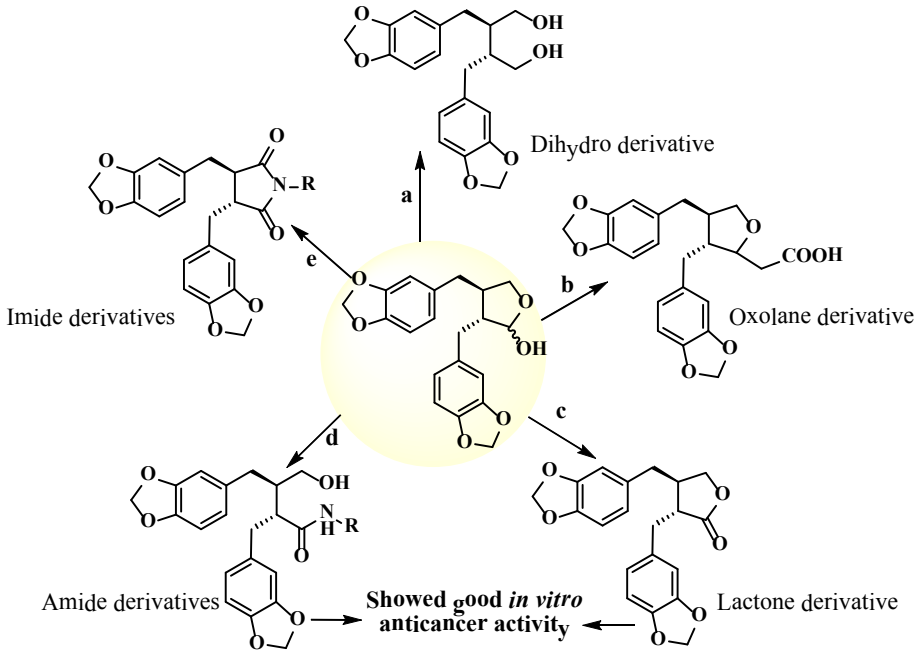


Figure 3: Structures of semi-synthetic derivatives of cubebin



Scheme 1: Reagents and conditions- (**a**) $NaBH_4$, MeOH, 0°C to r.t., 24h (**b**) i) PPh_3=CH-COOEt, dry toluene, reflux, 24h ii) Aq. NaOH (10%), MeOH, reflux, 3h (**c**) PCC, dry DCM, 12h (**d**) i) PCC, dry DCM, 12h ii) R-NH_2, dry THF, reflux, 36 h. (**e**) PCC, dry DCM, 12h

Recently we have carried out the synthesis of five different types of cubebnin derivatives containing lactone, dihydro, oxolane, amide as well as imide functionalities (scheme **1**). Cubebin and these semi-synthetic derivatives were tested for their *in vitro* anticancer activity against six human cancer cell lines (A549, K562, SiHa, KB, HCT116 and HT29) using MTT assay. Cubebin as well as its derivatives containing lactone and amide groups showed significant anticancer activity. Morphological analysis indicated that these compounds act through apoptosis mediated pathway of cell death.

4. Conclusion

Plants have been the source of medicine for wide spectrum of diseases all over the world. *Piper cubeba* berries are used for the treatment of many diseases in various traditional systems of medicine practiced across the globe. From the literature survey it is clear that *P. cubeba* is a rich source of many bioactive compounds, especially - lignans. Cubebin, the major compound isolated from the berries of *P. cubeba*, and its synthetic derivatives possess a wide range of bioactivities. Extensive research on cubebin and it semi-synthetic derivatives will definitely benefit the society in providing new drug leads in many major diseases areas such as cancer.

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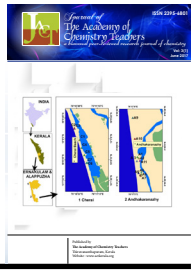

Study of Temporal and Spatial variation of Ground Water Quality along a Coastal stretch of Alappuzha District, Kerala, India: Post Tsunamic study

V. Sivanandan Achari*, T. Regi George, P Deepa and M S Ambili

School of Environmental Studies, Cochin University of Science and Technology, Kochi, Kerala - 682022

*Author for correspondence:

E-mail: vsachari@gmail.com

Abstract

Arattupuzha coast in Alappuzha is one of the tsunami affected coasts of India on 26th December 2004. In this study an attempt has been made to evaluate the temporal and spatial variation of important ground water quality parameters pH , Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Hardness (TH), Calcium, Magnesium, Sodium, Potassium, Bicarbonate, Chloride and Sulfate along the coastal strip of Alappuzha district by conducting sampling and analysis in each month of year 2012 and at the end of years 2013 & 2014.Comparison with WHO standards 2011 and BIS standards 2012 revealed that some of the sampling stations exceed the permissible limits in certain parameters. Comparative study of spatial distribution maps of water quality parameters generated using GIS revealed the temporal variation. Water Quality Index (WQI) calculated using these 11 parameters ranked good quality for dug well strata and excellent quality for bore well strata.

Keywords: Groundwater quality, Geographic Information System (GIS), Water Quality Index

Introduction:

Heavy ground water contamination was reported from Arattupuzha coast after the tsunami incident in 2004 December [1-3]. The present study was conducted with an objective to assess the current status of groundwater chemistry and water quality in the coastal area. Ground water composition is determined by atmospheric inputs, interaction of water with soil and rock and anthropogenic factors. The overexploitation of ground water in thickly populated coastal zones has detrimentally affected its quality and quantity and may result in negative water balance, triggering sea water intrusion.

The area selected for the present study (coastal area of Aartupuzha, Village) lies between North latitudes 9°7'41" & 9°11'26" and East longitudes 76°26'25" & 76°28'23" (Figure.1). The geomorphology of the area includes beach, mudflat, coastal plains and water body. The land use of the area includes agricultural field, mixed vegetation, built-up and water body. The area is a low lying coastal plain having a barrier island coast with a width about 50-200m and an elevation varying from 0 to1.5m above MSL. This coastal stretch is a permeable shoreline with a slanting plane. The slope of the area varies from 0^0 to 20.02^0. The soil texture of the area is sandy. The sand and silt is the litho logical feature of the study area. Fine to medium sands of Recent coastal alluvium mainly constitutes shallow phreatic aquifer and the thickness varies from a few metres to around 30m.

Materials and Methods:

Ground water samples were collected from 13 stations (7 bore wells and 6 dug wells) during each month of year 2012 and at the end of subsequent years 2013&2014. The important

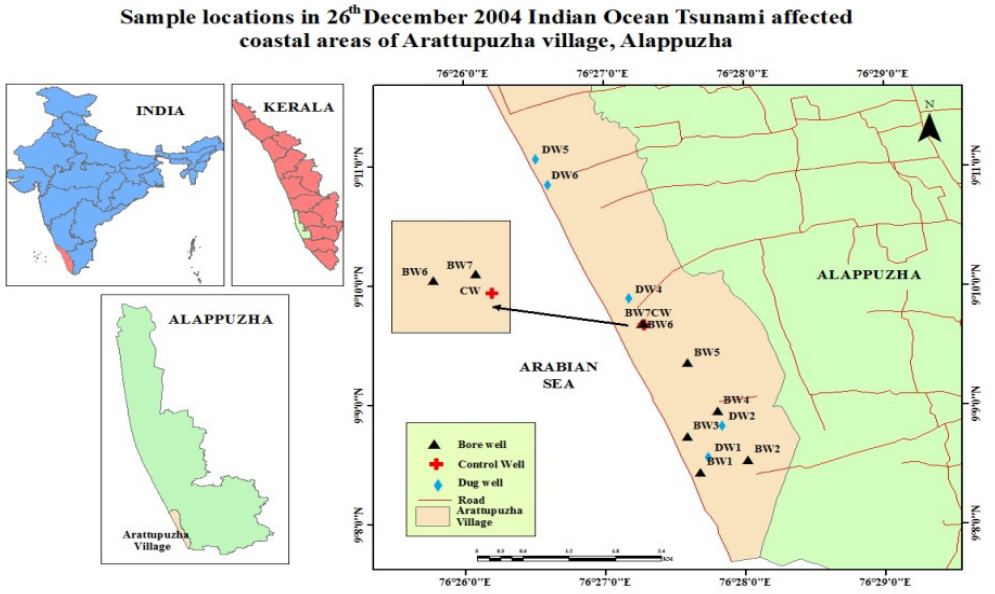

Figure.1: Location map of the study area

ground water quality parameters were analysed following standard procedures suggested by the American Public Health Association (APHA). Using Geographic Information System (GIS) spatial distribution of various parameters along the study area were plotted. Hydro chemical analysis can give the quality of the isolated patches only, but GIS maps can give the concentration at unknown points by using Inverse Distance Weighed (IDW) algorithm. IDW is a method of interpolation that estimates cell values by averaging the values of sample data points in the neighbourhood of each processing cell. The closer a point is to the centre of the cell being estimated, the more influence or weight it has in the averaging process. Water Quality Index(WQI) of the different water sources were evaluated by weighted Arithmetic Index method using the parameters pH, EC, Total Dissolved Solids (TDS), Total Hardness (TH), Ca, Mg, Na, K, HCO_3^-, Cl^- & SO_4^{2-}.

Results and Duscussion:

The average values of the important ground water quality parameters are given in Table (1) for dug well (DW) and bore well (BW) strata and they are compared with WHO and BIS standards. pH of water shows slight alkaline nature. It is due to the prominence of Bicarbonate ions. It also suggested lower dissolved organic matter content .That is only methyl orange alkalinity is present in water[4].

Table.1:Average values of the important Ground Water Quality parameters along the study area in various time periods

Parameter	April 2012		July 2012		December2012		December2013		December2014		WHO (2011)	BIS (2012)
	DW	BW	DW	BW	DW	BW	DW	BW	DW	BW		
pH	8.1	7.8	7.8	7.4	7.5	7.4	7.9	7.5	7.9	7.2	6.5-8.5	6.5-8.5
EC(mS/cm)	1.01	0.27	0.75	0.31	1.96	0.36	1.7	0.63	1.46	0.44	1.5	-
TDS (mg/l)	848	157	772	301	1345	113	536	96	832	212	500	500
TH (mg/l)	255	146	219	187	426	147	252	151	267	173	-	200
Ca (mg/L)	59	37	54.4	49	116	42	80	54	66	42	75	75
Mg (mg/L)	26.4	13	20	16	33	10	13	4	25	16	50	30
Na (mg/L)	56	15	47.8	18	177	23	119	21	141	24	200	-
K (mg/L)	13	6.2	10	6	16	6	14	6	12	6	12	-
HCO_3 (mg/L)	289	189	237	251	274	251	411	312	284	255	500	-
Cl (mg/L)	274	13.6	205	14	436	16	186	14	260	19	250	250
SO_4 (mg/L)	26	2	18	-	45	-	14	1.8	29	4.6	250	200

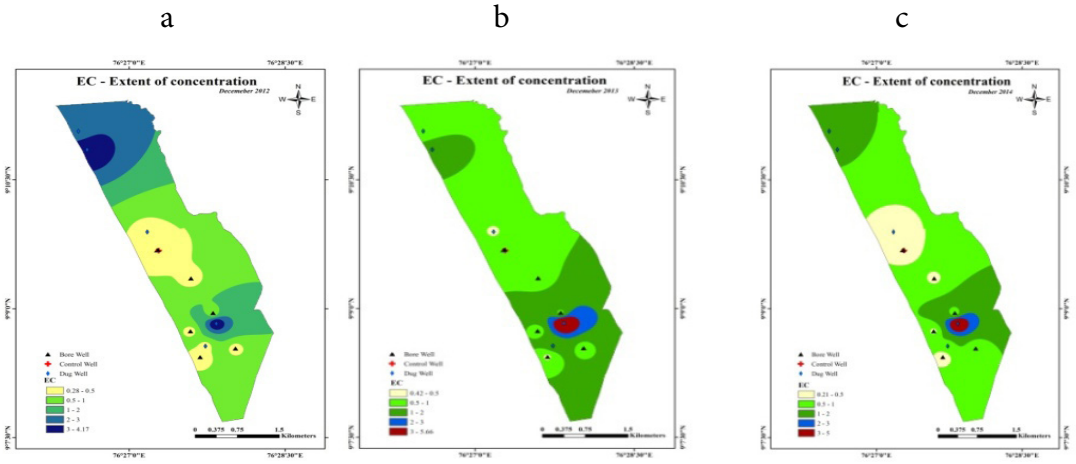

Figure.2: Spatial variation of Electrical Conductivity along the study area in a) 2012 December b) 2013 December and c) 2014 December

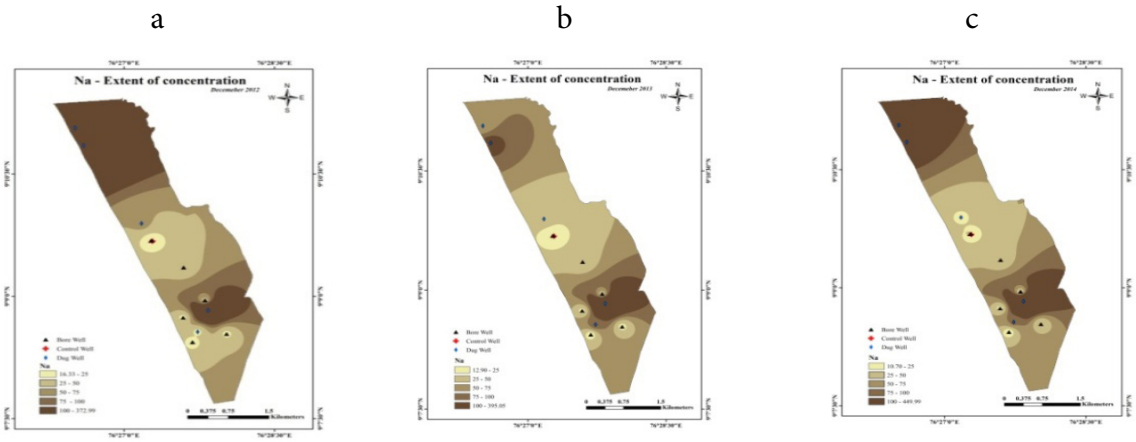

Figure.3: Spatial variation of Sodium (Na) along the study area in a) 2012 December b) 2013 December and c) 2014 December

Electrical Conductivity (EC), which is useful for the rapid assessment of salinity of coastal well waters, shows higher than standard value in December 2012 for DW strata. In April (Pre monsoon) the average value was 1.01mS/cm which decreases to 0.75mS/cm in July due to monsoon dilution and then increases in the post monsoon period to a value of 1.96 mS/cm in December 2012. The value decreases in the subsequent years. In December 2013 average EC value decreases to 1.7 and in December 2014 the value again decreases to 1.46mS/cm .

Spatial distribution maps also shows that in the northern shallow dug well stations sea water intrusion result in high EC values in 2012 December (Figure.2). There is a station with high EC value in the southeast side (4.18mS/cm in Dec. 2012, 5.68 mS/cm in Dec.2013 and 5.02 mS/cm in Dec. 2014) which indicate salinity. It is confirmed by the high values of TDS for DW strata, 1345mg/l in Dec.2012, 536mg/l in Dec. 2013 and 832mg/l in Dec. 2014 all are higher than standard limit. Calcite weathering shows moderate TDS values (500mg/l) but sea water intrusion leads to TDS values greater than 500mg/l. Sodium (Na) and Chloride (Cl^-) concentrations have a direct influence on salinity.

The average sodium concentration in DW strata is 177mg/l in Dec. 2012, 119mg/l in Dec. 2013 and 141mg/l in Dec. 2014. Although the average values are within standard limit, some of the stations exhibit higher concentrations (Figure.3). Sodium concentration is always higher than potassium concentration because potassium is more readily removed from solution by plants and clay minerals than sodium. Ion exchange reactions also increase the sodium concentration.

The average concentration of Chloride in DW

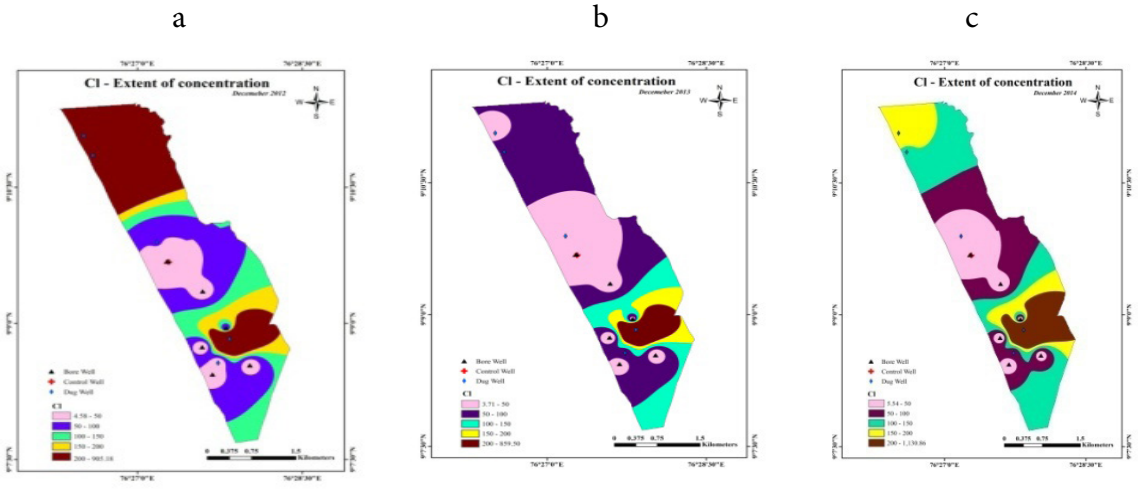

Figure.4: Spatial variation of Chloride (Cl^-) along the study area in a) 2012 December b) 2013 December and c) 2014 December

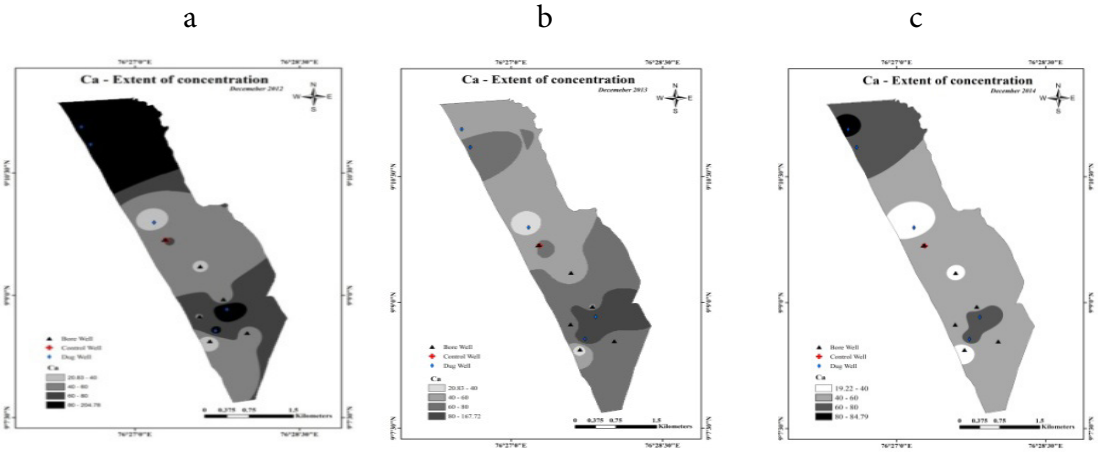

Figure.5: Spatial variation of Calcium (Ca) along the study area in a) 2012 December b) 2013 December and c) 2014 December

strata is 436mg/l in Dec.2012 and it decreases to 186mg/l in Dec. 2013and slightly increases to 260mg/l in Dec.2014. Primary source of Chloride in water is from sodium chloride directly from halite dissolution or indirectly from the ocean via rainfall. The higher concentration of Chloride ion is an index of pollution by salt water. These are observed in stations near to the sea (Figure.4). The higher concentration of chloride compared to sodium shows reverse natural softening.

On comparing the values of Total Hardness and Total Alkalinity it is observed that, in most of the samples TH is lower than alkalinity which shows that all hardness is temporary. Hardness is the sum of the Ca and Mg concentrations expressed in terms of mg/l of $CaCO_3$. The average value of TH in DW strata is 426mg/l in Dec.2012 which is higher than standard limit and the value decreases to 252mg/l in Dec.2013 and 267mg/l in Dec.2014. Hardness is an important parameter for determining irrigation suitability of waters.

Calcium, which is a prominent cation in natural water, has an average concentration 116mg/l in Dec.2012 for DW strata. It decreases to 80mg/l in Dec.2013 and to 66mg/l in Dec.2014. The higher Calcium concentration compared to Magnesium show weathering of sedimentary rocks other than dolomite. Spatial variation of Calcium concentration also shows higher values in certain areas (Figure.5).

Bicarbonate is an important anion in natural ground water. Its average value in DW strata is 274mg/l in Dec.2012 and increases to 411mg/l in Dec.2013 and decreases to 284mg/l in Dec.2014.

Table.2: Water Quality of Dug well and Bore well strata based on Water Quality Index values(mean of 6 dug wells and 7 bore wells)

Strata	2012December		2013December		2014December	
	WQI	Water quality	WQI	Water quality	WQI	Water quality
DW	83	Good water	79	Good water	78	Good water
BW	34	Excellent water	38	Excellent water	30	Excellent water

In Bore well (BW) strata the only prominent ion is Bicarbonate. The average value is 251mg/l in Dec.2012, 312mg/l in Dec.2013 and 255mg/l in Dec.2014. The increased concentration of Bicarbonate ion in Bore well water sources points to the dominance of mineral dissolution. Anyway all the bore well stations maintain good quality throughout the study period.

Water Quality Index (WQI) calculated using 11 parameters ranked good quality for dug well strata. Its average value is 83 in Dec.2012, 79 in Dec.2013 and 78 in Dec.2014. The average WQI values of BW strata are excellent quality for bore well strata (Table.2). In WQI the rating provide the composite influence of individual water quality parameters on the overall quality of water [8-10].

Conclusions:

A detailed study of the ground water quality of the coastal aquifers of Arattupuzha panchayath revealed that the major ground water quality parameters are within standard limit in most of the sampling stations except some shallow dug wells near the sea. The quality of water improved during the study period as revealed by Water Quality Index calculation.

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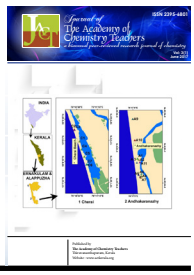

COMPUTER AIDED DRUG DISCOVERY – An Overview

Vijayalakshmi B[1]*, Sherin K[1], Sneha R Limbgaonkar[1] and Achuthsankar S Nair[1]

[1]*Department of Computational Biology and Bioinformatics, University of Kerala, Thiruvananthapuram, Kerala - 695581*

*Author for correspondence:

E-mail: vijayalakshmiajith@gmail.com

Abstract

The challenges in the health and disease management sector warrant a cumulative effort of researchers from multidisciplinary fields and Computer Aided Drug Discovery (CADD) are the latest technology adopted to analyse and address this issue. The strategy involves developing and designing a potential drug molecule that act as key to unlock specific molecular targets involved in the disease mechanism using computational resources. The drug candidate is selected and predicted from a given set of lead molecules by an iterative process involving comparative analysis of the conformations and energies of the drug-target complex generated during molecular docking. CADD has enabled a fast, easy and economic way of drug development that has been hitherto unseen in the pharma industry. This review provides an overview of the concept, methodology and resources related to this trend setting approach.

Keywords: CADD, Molecular docking, Lead/Hit, Molecular target, Disease mechanism.

1 Introduction

Chemistry has been considered as the 'central science' because of its pivotal role in linking several fields of studies in physical sciences, life sciences and applied sciences [1]. Chemistry is built on the laws of physics that govern particles such as atoms, protons, electrons, although chemistry cannot be fully reduced to quantum mechanics [2], as concepts such as the periodicity of the elements and chemical bonds are not defined by physics. In the same way, biology cannot be fully comprehended by chemistry despite the fact that the machinery that is responsible for life is composed of molecules, as concepts such as natural selection that are responsible for driving evolution do not come under chemistry.

Chemistry is fundamental to biology since it provides a methodology for studying and understanding the molecules that compose cells. Chemists study matter and its properties - the density, acidity, size and shape of molecules, while biologists want to understand living things and how they interact with their environment. Thus a conglomeration of various fundamental fields like mathematics, statistics, biology, chemistry and physics have to go hand in hand with the latest developments in engineering and technology to decipher the secret code of processes occurring in living organisms.

The universal entry of computers and informatics in almost every field, especially in the field of chemistry and biology has resulted in a plethora of solutions to address chemical and biological problems. The new age concept of problem-solving by an interdisciplinary and multidisciplinary approach is here to stay and the emerging research fields like bioinformatics, chemoinformatics, health informatics, medical informatics, clinical informatics are some of the new faces in this arena [4].

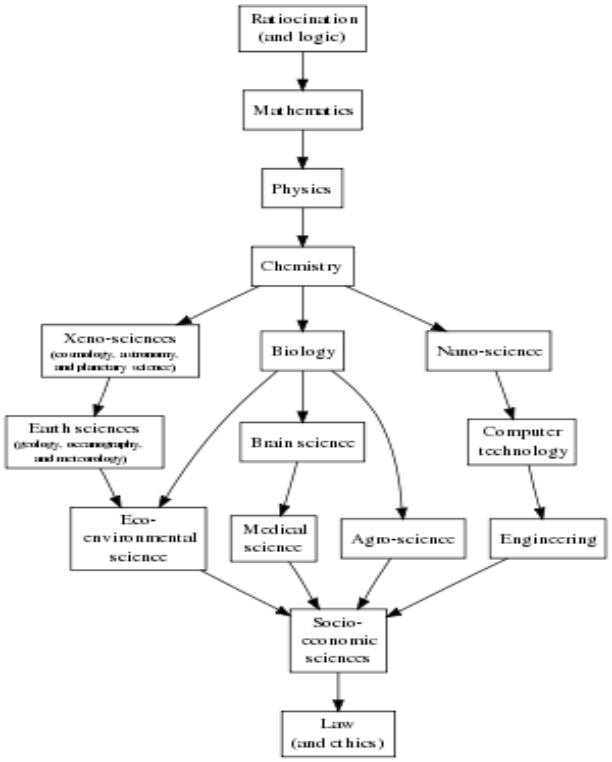

Figure 1: Chemistry as the "Central science" [3]

Drug discovery and development has for a long time been an outcome of serendipity, and this has been the prime reason for the minimal understanding and progress in this field. Further the process is also complex and highly risky considering the amount of time, money and resources being invested and hence for a long time been the monopoly of major pharma giants involved in the business. On an average, it takes 10-15 years and US $ 500- 800 million to introduce a drug into the market, with synthesis and testing of the lead being large contributor to the sum [5]. However, the advent of modern molecular approach to drug discovery and drug design, has led to several fold acceleration of the process of lead drug candidate (generally called the 'lead' molecule) identification in the pharmaceutical industry with greater accuracy and lesser cost. Computer Aided Drug Discovery (CADD) is the latest technology used by medical explorers to address the problem of health and disease management by computational simulation.

2 Modern approach to Drug Discovery

The modern approach to drug discovery is by a molecular approach wherein the mechanism behind ill-health or disease condition is explained based on the improper functioning of key macromolecules or cellular targets, which are to be aimed at for developing a potential drug. An overall view of the processes involved in drug discovery and development is shown in Fig. 2. The methodology involves generation of large repositories of molecular data related to diseases, pathways, DNA, RNA, proteins and small molecules.

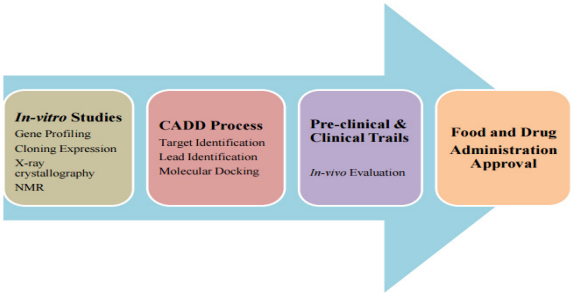

Fig 2 Drug discovery and Development Pipeline

Based on existing knowledge, computational models of molecular target associated with specific diseases and the drug candidate are predicted and their interaction is studied based on the calculation of energy associated with the molecules using the principle of molecular mechanics and molecular dynamics. The actual processes involved is far more complex and involves several mathematical, statistical and data analytical methods to nail down the best prediction model. Further the results are only empirical and hence are to be supported and validated by suitable experimental techniques.

3 CADD Concepts

The concept by which drugs act in the body against a disease or to improve health is explained based on the "lock and key" hypothesis proposed by E Fisher in 1894 based on the classical enzyme kinetics model [6]. This hypothesis assumes that the manifestation of disease involves key molecular targets in the body upon which the drug is to selectively act and produce the desirable change in health. Lock and key model specify the target and the binding ligand wherein the correct fitting of the 'lock and key' holds the solution to unlock the disease problem. The role of Quantitative Structure-Activity Relationship (QSAR) was investigated during the 1970s and the emergence of X-Ray crystallography, multi dimensional

NMR based molecular modeling and computer graphics in the 1980s paved way for development of several databases and softwares to accumulate and visualise 3D structures of proteins and small molecules [7]. Exploration of the human genome in the 1990s followed by the human proteome through bioinformatics, led to the growth of combinatorial chemistry, virtual screening, molecular simulation laying the foundation stones of CADD.

The basic idea of CADD is to study the interaction between a biological target that plays a key role in the disease pathway and a ligand that is administered as a drug to alleviate the disease condition. Definition for biological target and ligand has no strict boundaries and generally, the biological target may be a DNA, RNA or a protein molecule (Receptor, Enzyme, ion channel, transcription factor) while ligands are small molecules with molecular weight <1500 kDa and may be a protein, peptide, miRNA, lipids, metabolites, plant phytochemicals, semi-synthetic and synthetic drug molecules [8]. The major chunk of the CADD work is related to proteins as targets with small molecules as ligand or lead, mainly due to the significance of structural implication being prominent in the case of proteins.

The interaction of a ligand with a protein target may involve activation (agonism) or inhibition (antagonism) of the function of the protein. The computational simulation of this interaction study is called molecular docking wherein the associated energy of protein-ligand binding is determined for various conformational orientations to reach an optimum result. The binding of the ligand and the protein molecules relay on several parameters such as electrodynamic forces, Van der Waals interaction, electrostatic forces, dipole-dipole/ charge-dipole/charge-charge interaction, steric forces, entropy factor, solvent interaction, hydrogen bond and hydrophobic interaction [9]. Ultimately, molecular docking minimizes the free energy produced by the binding of ligand and protein target. The conformational adjustment of ligand and protein in order to serve the best fit is termed as induced fit. The best fit is necessary for the correct function of a particular target as incomplete complementarity may lead to dysfunction of the protein which causes serious health issues.

4 CADD Strategies

CADD can be classified into two categories based on the strategy adopted: Structure based and ligand based [10]. The most popularly adopted strategy, the structure based CADD relies on the structure of target protein, while the ligand based strategy is based on the chemical search for structural analogs by employing QSAR models. Structure based approach involves identifying lead molecules for a specific target that give the best fit from a large chemical space. Ligand based approach is adopted when the target structure is known and lead molecules are chosen based on the similarity of the structure and properties to a known ligand proven to be effective against specific therapeutic action.

4.1 Target identification and Structure determination

Selection of drug target is the prime factor that decides the success and failure of drug discovery. A thorough study of the disease pathway, gene expression are to be first made to understand the interplay between the proteins involved and choose a drug target that is unique or plays a key role in the disease mechanism. Further the chosen target should be able to be inhibited by a small molecule. The KEGG PATHWAY database is one large repository that caters to this need. The majority of current drug targets fall under the category of G-protein coupled receptors, nuclear receptors, ion channels, enzymes (*e.g.* kinases, proteases, deacetylases), chaperones, scaffolding proteins, transcription factors and transport proteins.

The next step after identifying the target is to obtain the 3D structure of the protein. Resources like Uniprot, PDB are storehouses of the protein data. Preferably the protein structures experimentally determined by X-Ray crystallography, NMR or Cryo-electron microscopy igh resolution structures of high resolution (low numeric value of resolution), with necessary domain regions are carefully chosen after thorough study of the protein molecule. In case the structure of the target

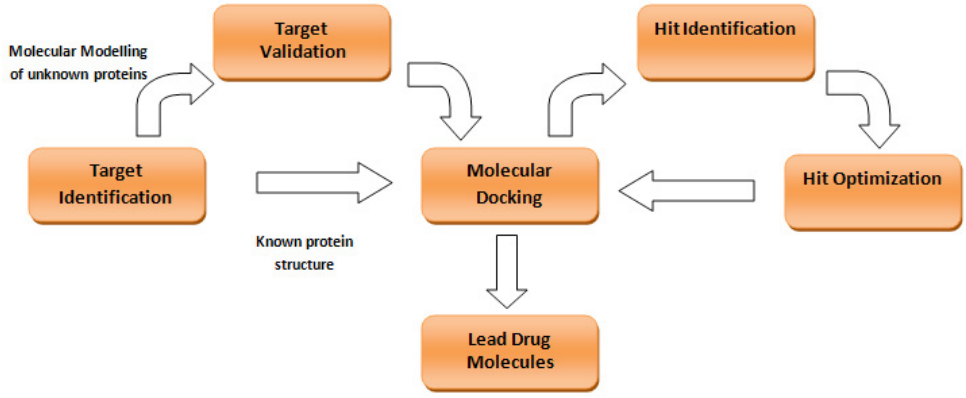

Fig 3: Structure based approach in CADD

protein is unavailable, CADD tools are available to generate the structure using protein sequence information. The method by which the unknown protein structure is determined by comparing sequence data with a known protein structure called the 'template' is called comparative protein modelling or template modelling. This includes (i) homology modelling, wherein the maximum sequence similarity is considered to choose the template and (ii) threading, wherein more than one template is chosen for the entire range of protein sequence. There is also another method called the d*e novo* or a*binitio* method for protein modelling which is template-free based on thermodynamic hypothesis and employs knowledge-based or physics-based methods to build the structure of the protein [11].

4.2 Hit/Lead identification and structure determination

'Lead' is the technical term used to refer promising drug candidates from amongst a given set of compounds called 'Hits', which bind to the protein target of interest and alters its function favourably. The lead can be retrieved from several public databases like PubChem, DrugBank available globally or may be user-defined based on the object of study or designed with the knowledge of protein complementarity. Several chemical structure drawing tools are also available to obtain structures of new molecules and convert them into 3D structures. Ligand molecules may also be subjected to several filtering methods to narrow down molecules that satisfy certain properties to be sustained as a good drug candidate. ADMET (Absorption, Distribution, Metabolism, Excretion and Toxicity) are one set of parameters used for screening ligands. Drug-likeness properties may be predicted using generalised rules like (i) Lipinski's Rule of 5: C log P value should not exceed more than 5, molecular weight should be less than 500 Dalton, not more than 10 hydrogen bond acceptor and not more than 5 hydrogen bond donors (4) (ii) BBB (Blood-Brain Barrier) Rule (iii) Veber rule [12].

4.3 Molecular Docking

Docking may be defined as the *in-silico* version of molecular interaction simulated by positioning different conformations of the ligand and the protein and predicting the best fit that generates a protein-ligand complex of minimal energy. When the docking is performed without conformational changes of the molecules, it is referred as rigid body docking, whereas flexible docking allows conformational changes of the molecules to identify the best fit [13].

Prior to performing the docking process the protein and the ligand molecules are cleaned and prepared to eliminate undesired atoms, molecules, charges and minimise the energy of the molecule. Virtual screening is the process of filtering or screening ligand molecules to find potential molecules with maximum affinity for a drug target when a large dataset of ligands are involved. The leads selected will be most suitable druggable molecule.

The docking software essentially employs a search algorithm to choose different conformation of the molecules by varying

rotatable bonds, bond bending, side chain orientation followed by evaluating the energy associated with a scoring function. Some of the widely used search algorithms are Monte Carlo algorithm, genetic algorithm, fragment based algorithm and molecular dynamics algorithm. Common scoring functions are classified into knowledge based, empirical and force-field based [11].

The best binding fit of the protein and the ligand is given in terms of energy score to determine the stability of the protein-ligand complex (usually higher the negative energy score better the stability) and are taken into consideration for further discoveries [14]. Once the molecular docking is done the drug candidates may be sent for preclinical trials followed by clinical trials for validation.

5 CADD Resources

The volume of information associated with diseases, disease pathways, genomic and proteomic sequence data of organisms (including pathogens like bacteria, virus, fungi etc), structural and physiochemical data related to proteins, metabolites and small molecules including plant phytochemicals, drug molecules etc is unbelievably magnanimous. Resources in CADD include web servers, databases, softwares and tools aid in storage, visualisation and manipulation of this data so as to make it accessible to researchers worldwide for a cumulative input in solving health issues.

5.1 Web Portals

Numerous web resources on computational drug discovery are available online. Web portals provide access to a large network of interconnected data and corresponding links to other resources and tools. Web portals of NCBI, Swiss Institute of Bioinformatics are providers of wide range of varied resources.

5.2 Databases

Databases are repositories of data related to gene and protein sequence, structural and physico-chemical properties of proteins and small molecules based on information collected from literature, reports based on experimental methods or results based on computational prediction methods. DNA sequence of different organisms is retrieved from databases like GenBank of NCBI, European Nucleotide Archive (ENA) of European Molecular Biology Laboratory (EMBL). GenBank contains nucleotide sequences for 370 000 formally described species. Protein Data Bank (PDB) is the popular archive of macromolecules from where structure of targets protein molecules is retrieved. Swiss-Prot and Protein Information Resource (PIR) also provide annotated protein sequences.

5.3 Softwares

Softwares used in CADD can be broadly categorised as molecular modelling softwares and docking softwares. Molecular modelling softwares are used to generate the 3D structure of ligands and proteins and for conversion of the structural files to specific file formats as required by the docking softwares. In case of small molecules, the 3D structures of molecules are generated from 2D structure drawn by tools like Marvin sketch, 2Dsketcher or ligand sketcher. In case of protein macromolecules with unknown structure, the 3D structures are generated from the protein sequence by homology modelling or *abinitio* modelling/ threading using tools like CPHmodels, MODELLER or SWISS-MODEL. The docking softwares perform a series of processes including virtual screening, ligand selection, ligand validation/optimization, and protein preparation, energy minimisation, binding site prediction, molecular docking and simulation. Several stand alone tools are available to perform these processes individually.

Softwares can also be classified based on availability and accessibility as open source and commercial softwares. Commercial softwares like Biovia Discovery Studio, Schrodinger provide customised and hassle-free operation of these tools but for a cost. Several free and open-access online softwares like Autodock, Swiss-model, Cluspro are also available. A selective list of web portals, databases, softwares and tools widely used in the field of CADD with their links and details are listed in Appendix.

6 CADD Drugs

The first approved drug developed based on CADD is Dorzolamide in 1995, which acts as a

Drug	Disease	Therapeutic action
Dorzolamide	Bilateral open angle glaucoma Ocular hypertension	Carbonic anhydrase inhibitor
Imatinib	Chronic myeloid leukemia	Tyrosine kinase inhibitor
Climetidine	○ Indigestion ○ Gastroesophageal reflux disease ○ Zollinger–Ellison syndrome ○ Gastritis ○ Heartburn· Peptic Esophagitis · Helicobacter Infections	Hydrogen receptor anagonist
Enfuvirtide	HIV/AIDS	HIV entry inhibitor
Raltegravir	HIV/AIDS	HIV integrase inhibitor
Zanamvir	Influenza	Antiviral drug

Table 1: Successful CADD based drugs in market

carbonic anhydrase inhibitor [32]. Imatinib, a tyrosine kinase inhibitor is another novel drug developed against cancer [33]. Cyclooxygenase based novel anti-inflammatory drugs, anti-cancer drugs against H-Ras proteins, anti-viral drugs especially against HIV are some of the drug categories widely studied based on CADD approach. Over the years several drugs have come into the market as an outcome of CADD application, some of which are enlisted in Table 1.

Conclusion

Success of computer aided drug designing depends on the validity of the modelled structures, tools used for predicting binding site, performance of docking algorithms, correctness in mapping the pharmacophore, accuracy of energy minimization and simulation algorithms, reliability of ADME and toxicity prediction tools, as well as on synthetic feasibility of designed inhibitor or drug. The wide scope of study on disease and its underlying molecular mechanism gives a better understanding of the problem under focus and this is the foremost advantage of employing CADD strategy for drug discovery. Secondly, the highly targeted approach in CADD increases the hit rate of finding a novel drug than traditional methods. The low cost and minimal resource requirement compared to chemical and biological experimental methods make CADD approach more attractive. However, false-positive and false-negative drug candidates during lead identification may often be misleading. Sampling of the correct molecular conformation of both ligand and receptor is also very much necessary and this needs both the domain knowledge and expertise in computing. Further multi-ligand interaction with a drug receptor, synergistic action of multiple ligands, multi-target interaction of a drug molecule are some of the future visions that are yet to be achieved. Inspite of the hurdles and challenges posed, CADD shows promising signs of progress due to the symbiotic interest exhibited by the academia and the industry alike to pool the knowledge resources and address the major health issues posed to humanity.

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Appendix

Web Portals		
Name	**Link**	**Details**
Computational Resources for Drug Discovery	http://crdd.osdd.net/index.html	CRDD is the *in silico* module of Open Source Drug Discovery (OSDD) an initiative by Council for Scientific and Industrial Research (CSIR), Govt. Of India, with a vision to provide affordable healthcare to the developing world.
Click2Drug	http://www.click2drug.org/	Click2Drug from Swiss Institute of Bioinformatics, provides details of resources and the softwares in CADD
National Center for Biotechnology Information	https://www.ncbi.nlm.nih.gov/	The National Center for Biotechnology Information (NCBI), National Institute of health (NIH), United States of America provides access to biomedical and genomic information.
ExPASy:SIB Bioinformatics resource portal	http://www.sib.swiss/	Resources Portal launched by the SIB Swiss Institute of Bioinformatics.

Databases		
Name	**Link**	**Details**
PubChem	https://pubchem.ncbi.nlm.nih.gov/	Structural and Physico-chemical data of Small molecules/metabolites
Chemspider	http://www.chemspider.com/Default.aspx	
ZINC [15]	http://zinc.docking.org/	
Dr. Duke's Ethnobotanical and phytochemical database	https://phytochem.nal.usda.gov/phytochem/search	Phytochemical data
TTD: Therapeutic target database [18]	http://bidd.nus.edu.sg/BIDD-Databases/TTD/TTD.asp	Drug and drug target data

GenBank, NCBI [16]	(www.ncbi.nlm.nih.gov/genba	Genomic Data
DNA Data Bank of Japan, (DDBJ)	(http://www.ddbj.nig.ac.jp)	
European Nucleotide Archive, European Molecular Biology Laboratory (EMBL)	http://www.ebi.ac.uk/ena	
European Nucleotide Archive (ENA)	(http://www.ebi.ac.uk/ena)	
Protein Data Bank, PDB	http://www.rcsb.org/pdb/home/home.do	Proteomic Data
UniProtKB/Swiss-Prot	http://www.ebi.ac.uk/uniprot	
Protein Information Resource (PIR)	http://pir.georgetown.edu/	

Software & Tools		
Name	**Link**	**Details**
MODELLER [19]	https://salilab.org/modeller/	Protein structure modelling
I-TASSER [20]	http://zhanglab.ccmb.med.umich.edu/I-TASSER/	
SWISSMODEL [22]	https://swissmodel.expasy.org/	
RaptorX [21]	http://raptorx.uchicago.edu/	
EsyPred [23]	http://www.unamur.be/sciences/biologie/urbm/bioinfo/esypred/	
Pre-ADMET [24]	https://preadmet.bmdrc.kr/	Ligand Property determination
QikProp [25]	https://www.schrodinger.com/QikProp	
ALOGPS [26]	http://www.vcclab.org/lab/alogps/	
PROCHECK [27]	http://www.ebi.ac.uk/thornton-srv/software/PROCHECK/	Protein Structure Validation
WHAT-CHECK [28]	http://swift.cmbi.ru.nl/gv/whatcheck/	
Ramachandran plot [29]	http://mordred.bioc.cam.ac.uk/~rapper/rampage.php or http://deposit.pdb.org/validate/	
CASTp [30]	http://sts.bioe.uic.edu/castp/	Binding Site prediction
MetaPocket [31]	http://projects.biotec.tu-dresden.de/metapocket/	
Autodock	(http://autodock.scripps.edu/)	Docking
AutoDock Vina [17]	http://vina.scripps.edu/	
GOLD	https://www.ccdc.cam.ac.uk/solutions/csd-discovery/components/gold/	
Schrodinger Maestro suite (MAESTRO; Schrödinger, LLC: Portland, OR, 2002.)	https://www.schrodinger.com/	
Discovery Studio from Accelyrs (Dassault Systèmes BIOVIA, 2017, San Diego: Dassault Systèmes, 2016.)	http://accelrys.com/products/collaborative-science/biovia-discovery-studio/	

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Groundwater Hydrochemical Facies of Tsunami Affected Alappad Coast of Kollam, Kerala, India

V. Sivanandan Achari*, M. S Ambili, C. A. Jaison, P. Deepa and T. Regi George

School of Environmental Studies, Cochin University of Science and Technology, Kochi, Kerala - 682022

*Author for correspondence:

E-mail: vsachari@gmail.com

Abstract

Alappad coast in Kollam district, the south-west coast of Kerala, India is one of the severely devastated areas by 26 December 2004 Indian Ocean Tsunami. This study discusses the hydrochemical facies of tsunami affected dug wells along this coastal segment after the tsunami impact from the year 2005, 2008, 2012 and 2014. The groundwater chemistry with respect to sodium chloride ratio, sodium adsorption ratio and salinity hazard were evaluated. The hydrochemical facies of the water sources has been saline water type with Na^{+}- K^{+} - Cl^{-} - SO_4^{2-} in 2005 and 2008. Studies conducted in 2012 shows the water behavior changed to temporary hardness water type with dominants of Ca^{2+}- Mg^{2+}- HCO_3 and continued to be same in 2014. Reverse ion exchange process in water sources analyzed in 2005 is the indication of salt water contamination and it gradually changed to ion exchange in 2012. On the basis of sodium adsorption ratio and salinity hazard water sources from 2012 are low sodium water with medium salinity which is suitable for irrigation.

Keywords: *Ground water quality, Alappad, Tsunami, Hill- Piper Trilinear plot.*

1. Introduction

Groundwater in coastal areas is under continuous treat by natural as well as anthropogenic activities. Population explosion has direct impact on groundwater sources especially where there are limited alternative sources. In village areas where there is no public water supply system, inhabitants depend solely on groundwater for their requirements.

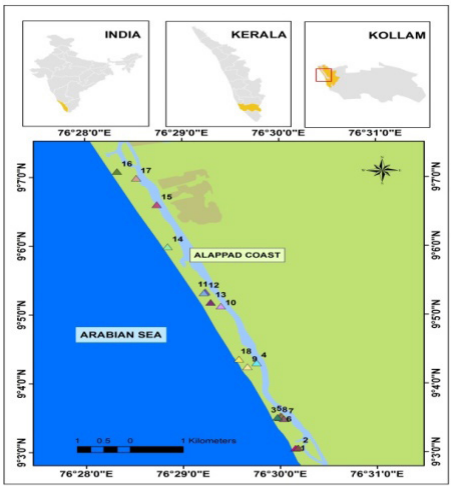

Figure 1: Location map and sampling stations

Alappad coast located between $9^0$2'57"N to $9^0$7'15"N latitude and $76^0$28'19"E to $76^0$30'13"E is economically significant area of the state of Kerala having extensive black sand mineral deposit and is a fast growing tourist destination. The geographical position of this narrow land between Arabian Sea and Kayamkulam estuary facilitated a clear swipe by giant tsunami waves in 26 December 2004. The groundwater quality in this area is completely degraded and it is continuously monitored from January 2005 just 7 days later this tsunami event [1-6].

2. Materials and methods

Ground water samples were collected from fifteen shallow dug wells in January 2012 and December 2014 and were compared with January 2005 and December 2008 data. Physico-chemical parameters of water samples such as pH, electrical conductivity (EC), total hardness (TH), total Alkalinity (TA), calcium (Ca), magnesium (Mg), chloride (Cl^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), iron (Fe), nitrate (NO_3^-), sodium (Na), potassium (K) and total dissolved solids (TDS) were analysed following the standard analytical procedures recommended by APHA (1998) to find the overall hydrochemistry of the region [7].

Hill-Piper Trilinear diagram is a combination of anion and cation triangles of equal sides that lies on a common baseline. The diamond plot between these triangles is used to designate different water types [8] demonstrating the relative composition of groundwater in terms of the anion-cation pairs. The piper diagram divides water into four basic types according to their position near the four vertices of the diamond plot. Water plotted at the top apex of the diamond is permanent hardness water type with high Ca^{2+} + Mg^{2+} and high Cl^- + SO_4^{2-} concentration. The water plots near left corner have high concentration of Ca^{2+}, Mg^{2+} and HCO_3^- and are a character of temporary hardness. Alkali carbonate water type is indicated at the bottom corner of the plot with high Na^++ K^+ and HCO_3^- + CO_3^{2-} concentration and the plot near the right corner represents saline water type high concentration of Na^++ K^+ and Cl^- + SO_4.

Sodium and chloride ions are the dominant cation and anion in sea water and its high concentration in groundwater is clearly an indication of sea water intrusion. Ratio of sodium and chloride ions is used to find the ion exchange process as a result of soil-water interaction. Salinity hazard of groundwater is the total concentrations of soluble salts and is determined using the measured electrical conductivity in micro Seimen (µS/cm). Water with EC value <250µS/cm is considered as excellent quality water and 250-750 µS/cm EC value are mediun or good quality. Electrical conductivity in the range 750µS/cm-2250 µS/cm is high salinity water (class III) and > 2250 is very high saline water [9].

Sodium adsorption ratio (SAR) is a measure of sodium in the water sample against calcium and magnesium ions. The formula for calculating sodium adsorption ratio is:

$$SAR = \frac{Na^+}{\sqrt{\frac{1}{2}(Ca^{2+} + Mg^{2+})}}$$

Where sodium, and magnesium are in milliequivalents/liter.

According to SAR, water is classified into low sodium to very high sodium water. Sodium hazard class S1 has SAR <10 (low sodium water). SAR in the range 10 to 18 is medium sodium water and it comes under sodium hazard class S2. Class S3 has SAR range 19 to 26 with high sodium water. SAR>26 are very high sodium water (S4).

3. Results and discussion

Figure (2) shows the piper plot for shallow dug wells in January 2005, December 2008, January 2012 and December 2014. The samples analysed in 2005 and 2008 are saline water type with high concentration of sodium and chloride ions. These water samples can be classified as Na^++ K^+ and Cl^- dominant type. High chloride concentration is due to contamination by tsunami waves [10]. The ground water samples collected in January 2012 and December 2014 are temporary hardness type and characterized by Ca^{2+}- Mg^{2+}- HCO_3^- with non-dominant cation and bicarbonate anion type.

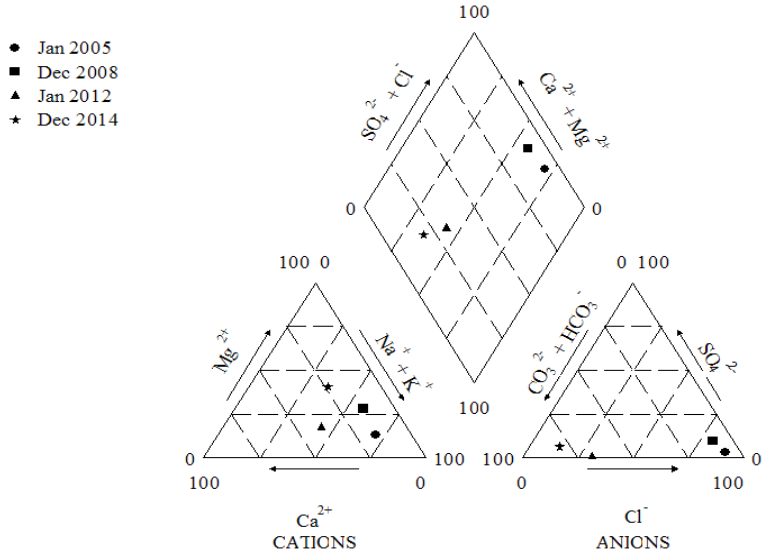

Figure 2: Hill Piper Trilinear plot of shallow dug wells of Alappad coast in the year 2005, 2008, 2012 and 2014.

The concentrations of sodium and chloride just after tsunami in January 2005 were about 70% and more than 80% respectively and in December 2014 nearly 10 years later it dropped down to less than 40% and 20% respectively. The variation in hydrochemical facies of groundwater in the course of time is shown in table below (Table 1).

Table 1: Variations in hydrochemical facies of shallow dug wells of Alappad coast in the study period

	Hydrochemical facies	Water Type
Jan 2005	Na^+-K^+-Cl^- -SO_4^{2-}	Saline
Dec 2008	Na^+-K^+-Cl^- -SO_4^{2-}	Saline
Jan 2012	Ca^{2+}-Mg^{2+}-HCO_3	Temporary Hardness
Dec 2014	Ca^{2+}-Mg^{2+}-HCO_3	Temporary Hardness

Sodium-chloride ratio of water sources in January 2005 and December 2008 shows reverse ion exchange ($Na^+/Cl^- <1$). Here Na^+ ions from water are get exchanged with Ca^{2+} and Mg^{2+} ions in soil. This is an indication of sea water intrusion. Water collected in January 2012 and December 2014 have $Na^+/ (Na^+ + Cl^-) > 0.5$ proposing the occurrences of ion exchange phenomena during the study period (Table 2).

Table 2: Na^+/Cl^- ionic ratio and probable inferences regarding groundwater quality of the Alappad region

	$Na^+/(Na^+ + Cl^-)$	Na^+/Cl^-	Inference
Jan 2005	0.33	0.48	Reverse ion exchange
Dec 2008	0.46	0.84	Reverse ion exchange
Jan 2012	0.58	1.48	Ion exchange
Dec 2014	0.68	3.66	Ion exchange

SAR is important measure in finding the quality and suitability of water for irrigation [11]. According to sodium adsorption ratio water samples collected after 7 days of Indian Ocean tsunami is medium sodium water with SAR 11.93. From 2008 to 2014 the water source is low sodium water with SAR less than 10 (Table 3).

Table 3: Quality of water with respect to SAR during the study period

	SAR	Sodium Hazard Class	Quality of water
Jan 2005	11.93	S2	Medium Sodium Water
Dec 2008	3.05	S1	Low Sodium Water
Jan 2012	2.06	S1	Low Sodium Water
Dec 2014	1.77	S1	Low Sodium Water

According to salinity hazard class water samples in January 2005 are classified as C4 class with very high salinity. In December 2008 this is reduced to Class 3 (C3) with reducing in EC from 7033.8 µS/cm to 825.0 µS/cm. Electrical conductivity again decreased to medium salinity hazard (Class 2) with 497.3 µS/cm and 587.3 µS/cm in January 2012 and December 2014 respectively.

Table 4: Salinity hazard classes and salinity index remark on water quality

	EC (µS/cm)	Salinity hazard Class	Salinity Index	Suitability
Jan 2005	7033.8	C4	Very high	Unsuitable
Dec 2008	825.0	C3	High	Doubtful
Jan 2012	497.3	C2	Medium	Good
Dec 2014	587.3	C2	Medium	Good

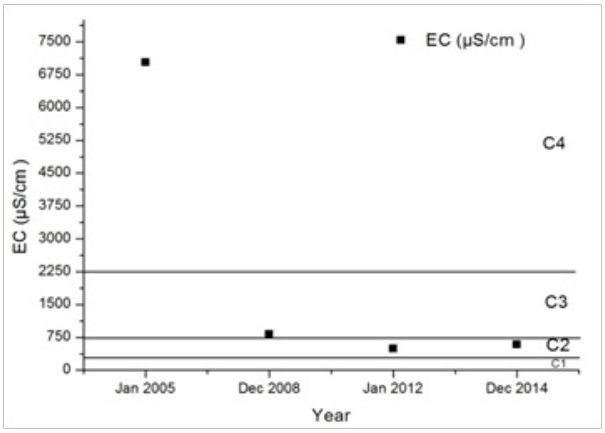

Figure 3: Electrical Conductivity (µS/cm) of the Alappad region during the study period

4. Conclusion

The hydrochemical facies of groundwater based on the Hill Piper trilinear plot just after tsunami event in January 2005 and for December 2008 is Na^+- K^+- Cl^-- SO_4^{2-} with saline water type whereas the water sources collected in 2012 January and December 2014 are Ca^{2+}- Mg^{2+} - HCO_3^- (temporary hardness water type). Due to inundation by sea water sodium chloride ratio of water in January 2005 shows reverse ion exchange process which gradually transformed to ion exchange process in January 2012. Ground water sources collected in 2005 and 2008 are unsuitable for irrigation with very high salinity with medium sodium hazard and high salinity with low sodium water respectively. Salinity falls down to medium salinity with low sodium hazard in January 2012 and continued as such in December 2014 which is suitable for irrigation.

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