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Heavy metal contamination and its indexing approach for river water

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ABSTRACT: The objective of the study is to reveal the seasonal variations in the river water quality with respect to heavy metals contamination. To get the extend of trace metals contamination, water samples were collected from twelve different locations along the course of the river and its tributaries on summer and the winter seasons. The concentrations of trace metals such as cadmium, cromium, copper, cobalt, iron, manganese, nickel, lead, mercury and zinc were determined using atomic absorption spectrophotometer. Most of the samples were found within limit of Indian drinking water standard (IS: 10500). The data generated were used to calculate the heavy metal pollution index of river water. The mean values of HPI were 36.19 in summer and 32.37 for winter seasons and these values are well below the critical index limit of 100 because of the sufficient flow in river system. Mercury and chromium could not be traced in any of the samples in the study area.
Keywords: Heavy metal pollution index; Industrial pollution; Seasonal variation.

INTRODUCTION

Recently one-pot synthesis emerged as an important tools in organic synthesis especially for heterocycic compounds, because of atom economy, simple and convenient and easy work-up procedures.Aminothiazoles is an important heterocyclic ring present in various bioactive molecules (Lewis J R 1999) and found to be best precursor of the preparation of various drugs like, antibacterial,(Tsuji, K. and Ishikawa, H.1944) antiinflammation,(Clemence, F et al.1988) antiallergies,(Hargrave, K. D et. al.1983) antihelmintic, antibiotic, and it also used on the treatment of schizophrenia.(Jaen, J. C et al. 1990) It also possesses inhibitors activity against enzyme cycloindependent kinase.(K. S. Kim et. al 2002).

Various methods have been employed for the synthesis of 4-phenyl-2-aminothiazoles ammonium-12-molybdophosphate in methanol,(Das, B et al.2006) β-cyclodextrin in water,(Narender, M et al.2005) iodine, (Siddiqui, H.L et al.2006) silica chloride,(Karade, H et al.2007) microwave energy,(Devendra S. Wagare et.al. 2016,) PEG-400-water,(Devendra S. Wagare et.al.2017) but, most of them suffering from various problems like, tedious work-up, used of hazardous precursors like alpha-halo ketones, iodines, bromines and poisonous catalyst as well as solvents and time consuming procedures. It prompted our interest to designed new rapid methods for the one-pot synthesis of 2-aminothaizoles in an environmentally friendly condition.

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We synthesized **8** derivatives of 4-aryl-2-aminothiazoles [3a-3h] using glycerol-water as a greener reaction medium under microwave irradiation to obtained excellent yield.(**scheme1**)

Scheme

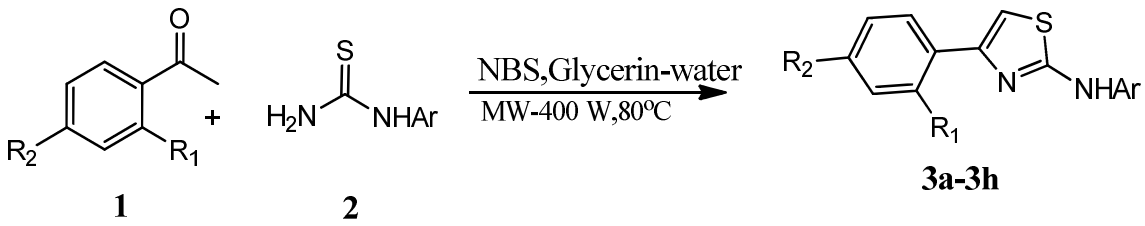

Fig.1 One-pot synthesis of 4-aryl-2-aminothiazole

EXPERIMENTAL SECTION

Material & Methods

The melting points of synthesized compounds were determined in open capillaries with the help of thermonic melting point apparatus and are uncorrected. The completion of reaction was monitored by thin layer chromatography (TLC) on silica gel G plates. The microwave synthesizer model (MAS-II) used for irradiation. The IR spectra were recorded on a Beckman Acuulab-10. Spectrometer (ν max in cm^{-1}) and the ^1H NMR spectra were recorded by Brucker DPX-400MHz using TMS as a references and $CDCl_3$ as solvent.

1. General Procedure for Preparation of Substituted 4-aryl-2-aminothiazoles (3b)

The mitxure of acetophenones (0.01mmol) and NBS (0.01 mmol) in glycerol and water (6 ml) irradiated for 1 minute and formation of α-bromoacetophenone monitored by thin layer chromatography. To this reaction mixture 2-chloro-phenylthiourea (0.01mmol) was added and irradiated for 1 min. reaction mixture poured on crushed ice and basified with ammonium hydroxide, residue obtained was filtered. The separated solid was recrystalised from aqueous ethanol.

Characterization data of some compounds

4-Phenylthiazol-2-amine (**3a**). Mp.148-151^{0}C (Lit.Ref.13 150-151 0C).
^1H NMR($CDCl_3$): d 4.94 (brs, 2H), 6.71 (s, 1H), 7.22-7.37 (m, 3H), 7.71-7.77 (m, 2H).; EIMS *m/z* (%): 177 (m+1100), spectral data consistent with Literature.[18,19]

2-(2-Chlorophenyl)amino-4-phenylthiazole 3b: 76-78^{0}C, lit.75-77 ^{0}C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 6.87 (1H, s, NH D_2O exchangeable); 7.31-8.31 (10H, m, Ar-H and thiazole proton). Anal. Calcd. for $C_{15}H_{11}ClN_2S$: C, 62.82; H, 3.87; N, 9.77; found C, 62.79; H, 3.84; N, 9.79,spectral data consistent with Literature.[18,19]

4-(4-chlorophenyl)-N-phenylthiazol-2-amine 3c 151-153^{0}C, lit.152-153 ^{0}C;

6.78 (br s, 1 H, NH, exchangeable with D2O), 6.80 (s, 1H, thiazole H), 7.37 (d, 2H, J = 8.6 Hz, ArH), 7.40–7.52 (m, 5H, ArH) and 7.76 (d, 2H, J = 8.6 Hz, ArH). spectral data consistent with Literature.[18,19]

2-(4-Chlorophenyl)amino-4-(4-chlorophenyl)thiazole 3d: 233-235^{0}C,

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lit.231-233 ^{0}C ^{1} HNMR (400 MHz, $CDCl_3$): δ 6.81(1H, s, NH D_2O exchangeable); 7.10-8.01(9H, m, C-H]. Anal. Calcd. For C15H10Cl2N2S: C, 56.09; H, 3.14; N, 8.72; found C, 56.07; H, 3.11; N, 8.74; spectra data was consistent with previous literature report.Lit. [18,19]

2-(4-Fluorophenyl)amino-4-(4-chlorophenyl)thiazole 3e:169-172 ^{0}C lit.169-170 ^{0}C; ^{1} HNMR (400 MHz, $CDCl_3$): δ 6.73(1H, s, NH D2O exchangeable); 7.11-8.01 (9H, m, Ar-H and thiazole proton at 5).. Anal. Calcd. for C15H10ClFN2S: C, 56.11; H, 3.31; N, 9.19; found C, 56.09; H, 3.29; N, 9.16 spectra data was consistent with previous literature report. Lit.[18,19]

4-(4-Bromophenyl)-Thiazol-2-amine 3f . Mp.164-166 0C (Lit.Ref.6 176-177 0C). ^{1}H NMR ($CDCl_3$): d 4.97 (brs, 2H, NH2), 6.73 (s, 1H), 7.50 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.0 Hz).;EIMS *m/z* (%): 257 (m+2 100), 255 (m+ 90), 149 (10).

2-(4-Chlorophenyl)amino-4-(4-bromophenyl)thiazole 3g: 141-142 ^{0}C lit.142^{0}C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 6.62 (1H, s, NH D_2O exchangeable); 7.21-7.74 (9H, m, Ar-H and thiazole proton). Anal. Calcd. for $C_{15}H_{10}BrClN_2S$: C, 49.27; H, 2.76; Br, 21.85; N, 7.66; found C, 49.23; H, 2.48; N, 7.54; m/z 366 (M+). spectra data was consistent with previous literature report.Lit. [18]

2-(4-Fluorophenyl)amino-4-(4-methylphenyl)thiazole 3h:105-107^{0}C lit.103^{0}C [18] ; ^{1} HNMR (400 MHz, CDCl3): δ 2.32 (3H, d, CH3); 6.67(1H, s, NH); 7.12 - 8.11 (8H, m, Ar-H); 8.01 (1H, s, thiazole H). Anal. Calcd. for C16H13FN2S: C, 67.58; H, 4.61; N, 9.85; found C, 67.54; H, 4.58; N, 9.84; spectra data was consistent with previous literature report.Lit. [18]

RESULT AND DISSCUSSION: On the onset of study, initially, we have tried reaction of acetophenones with NBS in glycerol under microwave irradiation and it was surprised that formation of phenacyl bromide in good yield. Synthesis of 2-aminothiazoles in glycerol already reported. So we approached towards one-pot synthesis of 4-aryl-2-aminothiazoles in glycerol. Again we tried same reaction in glycerol and water, yield of product increases with minimum reaction time. Glycerol is thermally stable solvent, keeping this in view, we tried this reaction under microwave and optimized reaction condition under different solvent ,it was observed that glycerol and water in 5:1 proportion best choice of solvent for this reaction. Entry 4.To generalised the scope of this protocol we synthesized **8** derivatives of 4-aryl-2-aminothiazoles using glycerol and water as greener solvent and result are shown in **table 2**. The yield was obtained in this method quite higher and reduced the time of reaction using microwave irradiation due to the good paired emerged of glycerol-water.

The IR spectra of (**3a-h**) showed absorption bands of the N-H in the range 3300-3580 cm-1 , there was a lack of strong stretching band at around 1680 cm-1of C=O of carbonyl of acetophenones. The ^{1}H-NMR spectra showed *singlets* at 7.68-7.78 ppm due to proton of the thiazole rings. these evidences confirmed that the thiazole ring had clearly been formed.

CONCLUSION: We have developed facile, expeditious, environmental friendly, microwave assisted, one pot method for the synthesis of 4-aryl-2-aminothiazole from easily available aromatic ketones and

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in-situ generated α-bromoacetophenone in glycerol and water (5:1) as a recyclable medium. Here we avoided unstable and hazardous α-chloro and α-bromocarbonyl compounds and organic, expensive catalyst and poisonous solvents.

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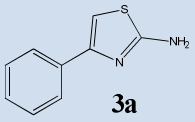
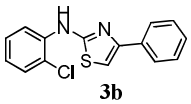
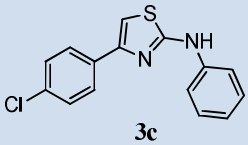
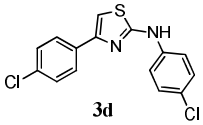
Table1. Optimization of solvent for the synthesis of 4-aryl-2-aminothiazole

Entry	Solvent	Reaction time	Microwave power	Yield[a] %
1	Solvent free	28 MIN.	400	00
2	Methanol	20 min.	400	60
3	Ethanol	25 MIN.	400	45
4	Glycerol	10 MIN.	400	84-89
6	Glycerol-water(1:1)	8 MIN.	400	81-87
7	Glycerol-water(3:1)	5 MIN.	400	85-90
8	**Glycerol-water(5:1)**	2-3 MIN.	400	91-98

[a]isolated yield

Table 2. Synthesis of 4-aryl-2-aminothiazole in glycerol-water

Entry	products	Mw. power	Time (sec.)	Yield[a] %
1	 **3a**	**400 watt**	**125**	**5**
2	 **3b**	**400 watt**	**110**	**97**
3	 **3c**	**400 watt**	**114**	**95**
4	 **3d**	**400 watt**	**115**	**97**

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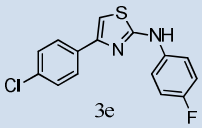
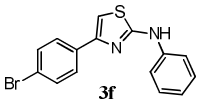
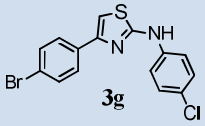
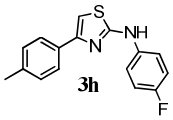
5	 3e	**400 watt**	**115**	**98**
6	 **3f**	**400 watt**	**120**	**97**
7	 **3g**	**400 watt**	**126**	**91**
8	 **3h**	**400 watt**	**128**	**93**

Reaction conditions: acetophenones (0.01 mmol), N-bromosuccinimide (0.01mmol) and thiourea (0.01mmol) in glycerol-Water (5:1) and microwave power at 400 watt at 80°C;
[a]Isolated yield

REFERENCES

Ball, P. H2O, A Biography of Water, Phoenix Press, London, England, **2000**.

Bellissent-Funnel, M.C, Done, J.C.; Hydrogen Bond Networks, Kluwer Academic Publications, Boston, MA,USA, **1994**.

Clemence, F. Marter, O.L. , Delevalle, F. Benzoni, J. Joua-nen, A. Jouquey, S. Mouren, M. Deraedt, R. ; J. Med. Chem.,**1988**, 31 ,1453.

Das, B. Reddy, V. Ramu, R ; J. Mol. Catal. A: Chem.,**2006**, 252, 235-237.

Devendra S. Wagare, Dinesh Lingampalle, Mazhar Farooqui and Ayesha Durrani; (2016); Der Pharma Chemica, 8 (1):408-411.

Devendra S. Wagare, Prashant D. Netankar, Mujahed Shaikh, Mazahar Farooqui, Ayesha Durrani, Environ Chem Lett.**2017,**15**,**3, 475-479

Dong, Jian Zhu.; Jiu-Xi, Chen.; Miao-Chang, Liu.; Jin-Chang, Ding.; Hua-Yue, Wu. *J. Braz. Chem. Soc.* **2009**, 20, 3, 482-487.

F. Wöhler, Ann. Phys.,**1828,** 37, 330-330.

George, W.K. Arjun, R.M. ; Tetrahedron Lett.,**2006**, 47, 5171-5172

Grieco, P.A. Organic Synthesis in Water, Ed, Blackie Academic and Professional, London,England, **1998**.

Hargrave, K. D.; Hess, F. K.; Oliver, J. T.J. Med. Chem.**1983**, 26, 1158–1163.
Head-Gordon, T. Hura, G. ; Chem. Rev., **2002**, 102, 2651-2670.

Jaen, J. C.; Wise, L. D.; Caprathe, B. W.; Tecle, H.; Bergmeier, S.; Humblet, C. C.; Heffner, T. G.; Meltzner,L. T.; Pugsley, T. A.J. Med. Chem.**1990**,33, 311–317.

Jain,K. S., Bariwal, J.B., Kathiravan, M. K. Raskar, V. K. Wankhede, G. S., Londhe, N.A., Dighe, Satish N.; Green and Sustainable Chemistry, 2011, 1, 36-40 doi:10.4236/gsc.2011.12007

Jawale Dhanaji V., Lingampalle Dinesh L., Pratap Umesh R., Mane Ramrao A.; Chinese Chemical Letters, **2010**, 21, 412-416

K. S. Kim, S. D. Kimball, R. N. Misra, D. B. Rawlins, et al., J. Med. Chem**.2002**,45, 3905–3927.

Karade, H. Sathe, M. Kaushik, M. ; Catal. Commun.,**2007**,8, 741-746

Lewis, J.R. ; Nat. Prod. Rep. **1999**,16, 389.

Li, C.J. , Chan, T.H. Organic reactions in aqueous media, Wiley, New York, USA,**1997.**

(a) Mahalle, S.R., Netankar, P.D. , Bondge, S.P. , Mane, R.A. ,Green Chem. Lett. Rev.,**2008**, 2, 103-106; (b) Pratap, U.R. Mali, J.R. Jawale, D.V. Mane, R.A. ; Tetrahedron Lett.,**2009**,50, 1352-1354; (c) Mali, J.R. Pratap, U.R. Netankar, P.D. Mane, R.A.; Tetrahedron Lett.,**2009,** 50 , 5025-5027.

Narender, M. Reddy, M. Sridhar, R. ; Tetrahedron Lett., **2005**, 46, 5953-5955.

Potewar, T.M , Ingle, S.A. Shrinivasan, K.V. ; Tetrahedron.,**2007**, 63, 11066-11069.

Sangeeta, B.; Anita, C. *Inter. J. Pharm. Pharm. Sci. (IAS)*, **2014**, 6, 6, 353-357.

Siddiqui, H.L., Iqbal, A. Ahmed, S.; Molecules.,**2006**, 11,206-211

Tsuji, K. Ishikawa, H. Biorg. Med. Chem. Lett.,**1944**, 4 ,1601

Wagare D.S., Mazhar Farooqui, Tushar D. keche, Ayesha Durrani; **2016**; synthetic communication, 46, 1741-1746. Doi: http://dx.doi.org/10.1080/00397911.2016.1223314

Zhang-Gao, Le; Zong-Bo, Xie.; Jian-Ping, Xu. *Molecules.* **2012**, 17, 13368-13375.