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### Biogenic synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles for ipso-hydroxylation of boronic acid in water

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#### Abstract

Here, biogenic synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles using fruit extract of *Zanthoxylum rhetsa* is reported. The SiO<sub>2</sub> nanoparticles was synthesized using paddy straw which is a by product obtained in cultivation of rice. The composite was characterised by spectroscopic method like XRD, SEM, TEM and EDX analysis. The *ipso*-hydroxylation reactions were carried out with excellent yield within a moderate time period with mild reaction condition in all cases. Therefore, this approach may be considered as simple, easy, cheap and greener, environment friendly protocol for *ipso*-hydroxylation of arylboronic acids at 50°C temperature.

Key words: Green synthesis; Nanoparticles; Biomaterials; ipso-hydroxylation

### 1. Introduction

In recent years, the development of greener, efficient, simple, eco-friendly and easy reaction methodologies play a major role in organic chemistry, in industry as well as in the academic world. <sup>1</sup> The attempt to find simple, environmentally benign methods in organic synthesis led to an enormous increase of research activities in the field of green chemistry <sup>2-3</sup>. In this regards, Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles was synthesised using fruit water extract of *Zanthoxylum rhetsa*. It is a very simple, easy, environment friendly and

cost effective method for synthesis of the  $Fe_2O_3@SiO_2$  nanoparticles. The SiO\_2 nanoparticles are synthesized using paddy rice straw. Further, the  $Fe_2O_3$  nanoparticles were loaded on SiO\_2 surface.

*Zanthoxylum rhetsa* is an important medicinal plant. It is used in the treatment of different diseases like dyspepsia, bronchitis, toothache, asthma and rheumatism. The fruit is use as fish poisoning fruit by indigenous people of Arunachal Pradesh <sup>4</sup>. The presence of phenolic acids and flavonoid compounds in the fruit extract may be responsible for the synthesis of  $Fe_2O_3$  nanoparticles. <sup>5</sup> Due to presence of such class bioactive compounds, it is used for synthesis of  $Fe_2O_3@SiO_2$  nanocomposite.

Phenol and its derivatives are present in various natural products like aromatic steroids, macrolides, quinines, terpenoids, alkaloids etc<sup>6</sup>. Phenols and poly phenols are used as anti-oxidant. <sup>7</sup> In general, phenols are prepared through the nucleophilic substitution of an aryl halide using different catalysts like copper, palladium etc. <sup>8</sup> which suffer from several drawbacks like harsh reaction condition, poor functional group compatibility, less substrate scope. Over the last few decades, phenylboronic acids and their derivatives have considered an important moiety in a wide range of organic reactions. <sup>9</sup> It is also used for the preparation of phenol with catalysts like copper, <sup>10</sup> (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> <sup>11</sup>, I<sub>2</sub>, <sup>12</sup> iron(III)oxide, <sup>13</sup> hydrazine hydrate, <sup>14</sup> potassium peroxymonosulfate, <sup>15</sup> Amberlite IR 120 resin <sup>16</sup> H<sub>3</sub>BO<sub>3</sub>–H<sub>2</sub>O<sub>2</sub>, <sup>17</sup> NaClO<sub>2</sub> <sup>18</sup> supported silver nano particle <sup>19</sup>, WERSA <sup>20</sup> etc.

It was observed that  $SiO_2$  is a nonporous material having large surface area. It is used as a supporting agent due to its large surface area. Beside this, the other advantages are- easy surface modification and can be recovered using simple method from the

reaction medium. It is a non toxic material which can be economically used and no effect on environment  $^{21}$ .

The basic objective in this study is to synthesis of biogenic  $Fe_2O_3@SiO_2$ nanoparticles using natural resources which can be utilised as very efficient catalyst for *ipso*-hydroxylation of some phenylboronic acid without using H<sub>2</sub>O<sub>2</sub> (Table 1) in presence of water. The reaction was moderately fast and completed within 2-5 hr at 50°C. To best of our knowledge, it is the first report of *ipso*-hydroxylation of phenylboronic acid using  $Fe_2O_3@SiO_2$  nanocomposite in water and oxygen from at 50°C.

#### 2. Experimental

#### 2.1. Synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles

For synthesis of  $Fe_2O_3@SiO_2$  nanocomposite, the fruit of *Zanthoxylum rhetsa* was dried and grinded and powdered. About 5 gm of the powder of fruit was added into 30 ml of distilled water for extraction. The extract is kept for 10 hr at room temperature and filtered it. Further, 5 ml 1mM FeCl<sub>3</sub>.6H<sub>2</sub>O was added to the filtrate of extract and stirred for 10 min. Finally, brown precipitate was formed. The precipitate was further filtered, washed and heated for 3 hr at 140°C for the formation of Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

#### 2.2. Synthesis of silica from rice paddy straw:

300 gm of the rice paddy straw was burnt. 5 gm of burnt ash was added in 100 ml of 2.5 M NaOH and the mixture was boiled for 4 hr. After cooling the mixture was filtered and treated with 5 M  $H_2SO_4$  acid solution. The P<sup>H</sup> of the solution was maintained around 8.5-9.0. As the result, white precipitation was occurred and the material was dried at 100°C for 3 hr to produce the silica (SiO<sub>2</sub>).

#### 2.3. Synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles:

Fe<sub>2</sub>O<sub>3</sub> nanoparticles were synthesized using *Zanthoxylum rhetsa* further loaded in the surface of SiO<sub>2</sub>. In this method, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were (1:12) refluxed in 15 ml methanol for 5 hr. The nanocomposite was then filtered and washed with methanol and water: methanol mixture (1:1) for 5-6 times. The composite material was dried at 100°C temperature for 2 hr. Finally, light brown nanocomposite Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> was formed.

**2.4. Characterization:** Fourier-transform infrared (FT-IR) spectra were recorded in the range of 400–5500 cm<sup>-1</sup> (Shimadzu Corporation, Japan). X-ray diffraction (XRD) analysis was carried out by Rigaku X-ray diffractometer (Model: ULTIMA IV, Rigaku, Japan). Scanning electron microscopy- Energy Dispersive X-ray (SEM-EDX) characterization was performed on JEOL JSM - 6360. The high resolution transmission electron microscopy (HR-TEM) images were recorded by a JEOL Model 2100 EX, Japan operated at voltage of 200 kV. Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Nuclear Magnetic Resonance (NMR) spectra were recorded by Advance DPX 500 MHz FT-NMR Spectrometer, (Make Bruker).

#### 2.3. General procedure for oxidation of boronic acid:

In a round bottomed flask 1 mmol phenyl boronic acid, and 4 mg of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> in 4 ml of the H<sub>2</sub>O were taken and stirred at room temperature for appropriate time. Progress of the reaction was monitored by TLC. After completion of the reaction mixture was extracted with Ethyl acetate. Further, the organic layer was separated and dried with sodium sulfate. The mixture was concentrated in rotary evaporator and product was purified by column chromatography. The product was analyzed by taking <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The recyclability test was done for catalyst  $Fe_2O_3@SiO_2$  up to 5<sup>th</sup> times. In this case, the catalyst was filtered and washed with water ethanol mixture 2/3 times. After washing it was reused for evaluate its catalytic activity.

#### **3. Results & Discussion**

#### 3.1. Characterization of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles

It is a very simple, eco-friendly method for biogenic synthesis of  $Fe_2O_3$  nanoparticles using the fruit extract of *Zanthoxylum rhetsa*. In this case, the fruit extract of *Zanthoxylum rhetsa* was added in  $FeCl_3 \cdot 6H_2O$  solution for formation of  $Fe_2O_3$ nanoparticles. In this process, the reduction took place  $Fe^{3+}$  to formed  $Fe_3O_4$ . The functional group (C=O) of phenolic acid or the flavonoid of extract may co-ordinated with  $Fe^{3+}$  ion to form ferric protein chains, The HO----Fe<sup>3+</sup> bond further transformed to formed  $Fe(OH)_3$ . Accordingly, on slow evaporation,  $Fe(OH)_3$  is dehydrated (-H<sub>2</sub>O) when heated at 160°C in presence of oxygen to produced  $Fe_2O_3$  nanoparticles. It is clearly supported by reported information <sup>21</sup>.

The supporting agent i.e.  $SiO_2$  nanoparticles were also biosynthesized from rice paddy straw which is a waste material or by product produced during cultivation of rice. The SiO<sub>2</sub> nanoparticles were characterized by SEM and TEM analysis. The SEM image revealed the formation of the flake sheet of SiO<sub>2</sub> [Figure 1S (A), supporting information (SI)]. The TEM image revealed the formation of pentagonal, hexagonal sheet overlap each other [Figure 1S (B), SI].

The  $Fe_2O_3@SiO_2$  nanoparticles was further characterised by basic spectroscopic technique such as XRD, SEM, EDX and TEM analysis. In XRD analysis, the diffraction peaks appeared at 20 value 36.4°, 44.8°, 53.9°, and 63.6° were assigned to (311), (400),

(422), and (440) reflection in the unit cell respectively, which revealed the spinal structure of  $Fe_2O_3$  (JCPDS Card No.19–0629). The corresponding spacing i.e. 'd' value of  $Fe_2O_3$  nanoparticles are 2.48, 2.42, 2.02 and 1.48 respectively (Figure 1).

sub-orth





The SEM analysis revealed the formation of sheet like morphology of  $Fe_2O_3@SiO_2$  nanocomposite which overlapped randomly (Figure 2A-B). This basic morphology consists of small  $Fe_2O_3$  nanoparticles decorated on SiO<sub>2</sub> surface. It was difficult to examine the surface image using SEM analysis. So, it was further examined by HR-TEM analysis.





(B)



Figure 2: (A-B) SEM (C-D) TEM images of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocomposite

The shape and size of the nanoparticles was further studied by HR-TEM analysis. The HR-TEM results indicated the formation cluster like  $Fe_2O_3@SiO_2$  nanocomposite. It also observed that most of  $Fe_2O_3$  nanoparticles was dispersed on the surface of SiO\_2 (Figure 2C-D). But it was not in symmetric pattern. The size of the nanoparticles was found in the range of  $5.0\pm0.3 - 21.0\pm1.4$  nm. The average size of the particles was  $12.2\pm0.8$  nm. It was supported by dynamic light scattering (DLS) study (Figure 2S, SI).

The EDX analysis was carried out for further evidence of  $Fe_2O_3@SiO_2$  nanoparticles. This analysis showed that weight % of O, Si and Fe are 62.28, 33.81 and 3.91 and atomic % is 75.34, 23.30 and 1.36 respectively. It strongly supported the presence of Fe, O and Si elements respectively in nanocomposite (Figure 3S, SI).

From the literature, it was found that the  $H_2O_2$  is used as oxidant in *ipso*-hydroxylation reaction.<sup>15, 17</sup> Different type strong bases, ligand were used for activated the  $H_2O_2$  in nucleophilic substitution. But there are some disadvantages in using strong bases and drastic reaction condition. To avoid such condition a very simple, economic, green easy method was used for oxidation of phenylboronic acid to phenols without using

 $H_2O_2$ . So, it has a significant scope in utilization of  $Fe_2O_3@SiO_2$  catalyst for *ipso*-hydroxylation reaction in water.

#### 3.2. Optimization of reaction condition

Further optimization was carried out in water at temperature 50°C in presence of air for conversion of phenylboronic acid is considered as model system. The optimization results are depicted in Table 1. Initially the amount of the catalyst was optimized. In this study, the mount of catalyst was varied from 1.0 to 5.0 mg in presence of water at 50°C. It was observed that the performance of the reaction was best when 4 mg of catalyst was used. The yield was found 98% in 2 hr at 50°C. The reaction was carried out with a mild condition. As the results, lesser toxic, eco-friendly, simple, cost effective method was observed with excellent yield. This makes this *ipso*-hydroxylation as one of the cleanest and greenest alternative protocol.

Sl No	Amount of catalyst (mg)	Time (hr)	Yield (%)
1	1.0	8	70
2	2.0	5	92
3	3.0	5	94
4	4.0	2	98
5	5.0	2	98

Table 1: Optimization of amount of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> catalyst in presence of water at 50°C.

Moreover, the reaction condition was optimized further by changing the other condition like catalyst/solvent/base etc. (Table 2). We tried different type of solvent like methanol, butanol, water, ethanol etc. Here, the water was found the best solvent in this system. After optimization, the reaction was carried out in presence of different electron

donating and withdrawing group as well as hetero atom, aliphatic, benzene diboronic acid and arylboronic acid.

Further the reaction was carried out without catalyst. It was observed that no product was formed without the catalyst. So, phenol was not formed in presence water only in this reaction. Further reaction was carried out in anhydrous condition. The product was formed in this experiment. But yield was very low i.e. 41%. The *ipso*-hydroxylation reaction also carried out in inert condition also. In such case, no product was formed. It indicated that oxygen from air may participate in formation of phenol along with water in this study <sup>22</sup>.

Table 2: Optimization of solvent in presence of 4 mg of  $Fe_2O_3@SiO_2$  catalyst in water and in formation of phenol from phenylboronic acid

Sl No	Solvent	Time (hr)	Yield (%)
1	CH <sub>3</sub> OH	2	55
2	C <sub>2</sub> H <sub>5</sub> OH	2	60
3	C <sub>4</sub> H <sub>9</sub> OH	2	75
4	H <sub>2</sub> O	2	98
5	$H_2O$ : $CH_3OH$	2	95

As per our protocol, the reactions were carried out very smoothly and converting various substrates of electron-donating and withdrawing groups bearing phenylboronic acids to phenols with very good to excellent yield (Table 3) in mild reaction condition.

 Table 3: Oxidation of different boronic acid <sup>a</sup>



Entry	R	Time (hr)	Yield <sup>bc</sup>
1	Н	2	98
2	4-Cl	2	96
3	4-Br	3	95
4	4-OMe	4	91
5	3-Me-4-OMe	3	93
6	4-t-Butyl	4	95
7	3-OMe	4	90
8	3-NO <sub>2</sub>	3	94
9	2-NO <sub>2</sub>	4	93
10	4-NO <sub>2</sub>	5	92
11	4-CHO	3	90
12	1- Pyrene	5	88
13	4-Dibenzofuran	3	90
14	2-9H-Fluoren	4	90
15	6-2,3-	4	91
	Dihydrobenzo[b][1,4]dioxin		
16	2-ОН	3	86
17	3-ОН	3	89
18	4-OH-2-mercapto pyrimidine	4	88
19	1-Octyl	3	92
20	Cyclohexyl	3	91

<sup>a</sup> Reaction conditions: phenylboronic acid (1 mmol), Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> (4 mg), Water (4 ml) <sup>b</sup> Isolated yield. <sup>c</sup> All compounds are characterized by <sup>1</sup>H & <sup>13</sup>C NMR spectroscopy

It was observed that substrate containing electron withdrawing groups were more efficient than electrons donating groups in hydroxylation reaction (Table 3, Entry 1-11). Moreover, single aryl ring system boronic acid is more effective then the double/triple

phenyl ring system of boronic acid in terms of conversion to phenols with respect to time and yield (Table 3, Entry 12-15). Further, the hydroxylation was carried out for diboronic acid, heterocyclic ring and aliphatic or aliphatic cyclic system (Table 3; Entry 16-20). In case of phenyldiboronic acid the reaction was carried out with 1,2-phenyldiboronic acid (Table 3; Entry 16) and 1, 3-phenyldiboronic acid (Table 3; Entry 17) with same reaction condition. In both cases product was formed with 86% yield of 1, 2-dihydroxybenzene and 89% of 1,3-dihydroxy benzene respectively. The lower yield of 1,2-dihydroxy benzene may be due to presence of two bulky group[-B(OH)<sub>2</sub>] in 1,2 position. So, it is clear that overall yield of the product is comparatively low if the reactant is a diboronic acid. Another product i.e. 4, 6-dihydroxy-2-mercapto pyrimidine (Table 3, Entry 18) was formed from respective diboronic acid with moderate yield (88%). The presence of heteroatom ring system has no significant role in this study. In case of aliphatic chain or cyclic system (Table 3, Entry 19-20) high yield was observed (91-92%). The aliphatic boronic acids are easily converted to respective alcohol.

Till today, there is no earlier report on *ipso*-hydroxylation using such a mild, simple, eco-friendly, green, efficient and economic reaction condition using  $Fe_2O_3@SiO_2$ in presence of water and air. Therefore, this seems to be a very efficient protocol with a wide range of substrate scope for *ipso*-hydroxylation of phenylboronic acids to phenols. All the <sup>1</sup>H and <sup>13</sup>C NMR analysis data are reported in scheme 1S

The recyclability of  $Fe_2O_3@SiO_2$  nanoparticles was tested by considering phenylboronic acid as model substrate in *ipso*-hydroxylation reaction. The recirculation of catalyst was done by simple filtration method. The recovered catalyst was wash with water and water ethanol mixed solvent (1:1). Then the recovered catalyst reused for

further reaction. It was confirmed that efficiency remain almost same after five times recycle of catalyst (1<sup>st</sup> recycle 98%, 2<sup>nd</sup> recycle 97% and 3<sup>rd</sup> recycle 96%, 4<sup>th</sup> recycle 94% and 5<sup>th</sup> recycle 95% phenylboronic acid was obtained) (Figure 4S, SI). After completion of the reactions, products were extracted with diethylether and Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> separated by filtration and washed with water/ethanol and reused. Thus we can consider Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> as a reusable heterogeneous catalyst. The TEM and XRD image showed that the morphology and size distribution of the Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocatalyst remain almost same after use of 5<sup>th</sup> cycle of catalytic reaction [Figure 5S A-B, SI].

The reusability of the catalyst further investigated with precise evidence through N<sub>2</sub> adsorption–desorption study. It was found that the BET surface area and total pore volume of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> was 6.174 m<sup>2</sup>/g and 0.1143 m<sup>3</sup>/g respectively for the fresh catalyst. Moreover, it was found that the total specific surface area of the catalysts after 5<sup>th</sup> cycle decrease significantly to 134 from 223 m<sup>2</sup> g<sup>-1</sup> of fresh catalyst [Figure 6S, SI]. The reduction of the surface area of the catalyst may be due to the partial degradation of the support. The adsorption–desorption hysteresis loop of the catalyst shifted in the range P/P<sub>0</sub> = 0.30 and 0.90 to P/P<sub>0</sub> = 0.45 and 0.84 used after the 5<sup>th</sup> run respectively. The changed of the loop of the curve may be due to the change in the structure of pores. The BJH pore size distribution curve of the catalyst after 5<sup>th</sup> cycle shows a slight widening of the distribution pattern compared to fresh catalyst [Figure 7S, SI]. However, it is strongly supported that there is no loss of efficiency of the catalyst after 5<sup>th</sup> recycle.

The extract mechanism of the *ipso*-hydroxylation of phenylboronic acid is not known. Therefore we proposed a plausible mechanism for *ipso*-hydroxylation of phenylboronic acid to phenol in presence of  $Fe_2O_3@SiO_2$  (Scheme 1). The reaction was take place via

oxidative addition followed by reductive elimination of the boronic acid <sup>21</sup> in presence of  $H_2O$ . For further evidence, the preliminary mechanistic study was carried using isotopic labeled water ( $H_2O^{18}$ ) was performed. When the reaction was carried out using  $H_2O^{18}$  as solvent under optimal condition incorporation of  $O^{18}$  in phenol was observed [Scheme 2S]. So, it is observed that the oxygen source of phenol due to presence of water in the reaction mixture. It is also strongly supported by the reported data <sup>22-24</sup>. But, there may be a possibility to participate oxygen from the air in formation of phenol. The details of mechanism of the reaction are yet to study. Moreover broaden the scope of the substrate will be done. The reaction was occurs on the surface of the catalyst. After 5<sup>th</sup> cycle there is no significant change on the surface of the catalyst.





From the literature it was found that, the phenol can be synthesized using various methods with different reaction condition [Table 4]. It is compared with reported result <sup>25-</sup> <sup>30</sup>. But this is the simplest, easy, eco-friendly method for synthesis of phenol from

phenylboronic acid in water at 50°C. Moreover there is no any hazardous chemical like

 $H_2O_2$  was used in this study. This is the novelty of this study.

Table 4: A comparison between 'green-ness' among catalyst/reagents in the hydroxylation of phenylboronic acid to phenol with reported data and present work

Sl No	Catalyst	Oxidant	Time (min)	Yield (%)	Reference
1	$N_2H_4/Cs_2CO_3$	O <sub>2</sub>	60	94	25
2	Urea/MeOH	$H_2O_2$	5	97	26
3	Biosilica	30% H <sub>2</sub> O <sub>2</sub> (0.2ml)	5	93	27
4	WERSA	30% H <sub>2</sub> O <sub>2</sub> (0.2ml)	5	98	28
5	NH <sub>4</sub> HCO <sub>3</sub>	30% H <sub>2</sub> O <sub>2</sub> (1.1ml)	120	95	29
6	Cu <sub>2</sub> O	30% H <sub>2</sub> O <sub>2</sub>	10	96	30
8	Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub>	$H_2O/O_2$ from air	120	98	Present
					work
4 Conclusions					

#### 4. Conclusions

A simple efficient and inexpensive process of biosynthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocomposite was developed using Zanthoxylum rhetsa. The supporting agent i.e. SiO<sub>2</sub> extracted from rice paddy straw which is a waste material. Here, we have developed a very simple, green, mild and eco-friendly protocol for *ipso*-hydroxylation of arylboronic acids to phenols without using  $H_2O_2$  as oxidant in presence of biogenic Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocatalyst and air at 50°C. It is very simple, cost effective and compatible with various electron-donating and withdrawing groups. Further, there is lots of prospect and have significant advantages made in presence of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> a very adaptable and competitive catalyst system. So, it can be considered as clean and safer alternative for various other reactions system as well as in chemical industry in near future

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Acception

### Highlights

- Biosynthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles using Zanthoxylum rhetsa
- A highly efficient protocol for *ipso*-hydroxylation of phenylboronic acid to phenols
- The reactions were carried out without using strong base and hazardous organic solvent.

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• A new avenue for *ipso*-hydroxylation of phenylboronic acid in water.

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### **Graphical Abstract**

Biogenic synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanoparticles and its application in *ipso*-hydroxylation of phenylboronic acid to phenols in presence of water is reported here.

