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## PAPER



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## An environmentally friendly approach to the green synthesis of azo dyes in the presence of magnetic solid acid catalysts

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A solvent-free, efficient and green approach for the synthesis of azo dyes has been developed by the diazo coupling reactions of aromatic amines with  $\beta$ -naphthol in the presence of sulfonic acid functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H) by a grinding method at room temperature. This green methodology aims to overcome the limitations and drawbacks of the previously reported methods such as low temperature, use of acids, alkalis and toxic solvents, instability of diazonium salts at room temperature, modest yields, and long reaction times. Moreover, the attractive advantages of the process include mild conditions with excellent conversions, simple product isolation process, inexpensive procedure and recyclability of the magnetic catalyst.

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## 1. Introduction

In recent years, organic colour chemistry has been undergoing very exciting developments as a result of the opportunities presented by dye applications in modern technology fields such as linear and non-linear optics, reprography, electronic devices, sensors and biomedical uses.1 Azo dye compounds are the most widely used class of synthesized organic dyes due to their versatile applications in different fields such as dyeing textile fibers,<sup>2</sup> biological-pharmacological activities,3 organic synthesis<sup>4</sup> and as materials with excellent optic and photoelectric properties.5 Azo dyes are generally synthesized in two steps: the diazotization of aromatic primary amines, followed by the coupling reaction between diazonium salts and activated aromatic compounds (phenols or aromatic amines). The formation of diazonium salts starts with the protonation of nitrous acid under strongly acidic conditions and the azo coupling is carried out at low temperature  $(0-5 \ ^{\circ}C)$  in the presence of nucleophilic coupling components.6 The main limitations of this synthetic method are low temperature, use of acid-base catalyst, instability of aryl diazonium salts at room temperature, modest yields, and long reaction times. However, the main limitation of such synthetic processes is its environmental incompatibility. The acidic and basic effluents from the laboratory and industry result in permanent damage to the environment and disturb the ecological balance.6,7

Recently, solid acids have resolved these problems and improved activity and selectivity.<sup>6-10</sup> In this regard, nanostructure solid acids exhibit higher activity and selectivity than

their corresponding bulk materials. As the diameter of the particle decreases to the nanometer scale, external surface area becomes available for chemical transformations.<sup>11-13</sup> Among these, solid acid systems and magnetically recyclable catalysts are unique due to their inherent properties such as biocompatibility, thermal stability against degradation, easy renewability and recovery by magnetic separation, higher catalytic activity due to the higher loading of active sites and large surface area.14-16 Moreover, various solid acids have been used for the preparation of azo dyes compounds.17,18 Although satisfactory yields of products are usually obtained, some of these synthetic methods are not environmentally friendly and suffer from one or more drawbacks such as control of the reaction temperatures, difficult purification, unsatisfactory yields, and long reaction time.6,7 Therefore, the development of clean, high-yielding, mild, and green approaches is still a challenge for diazotization and diazo coupling reactions.

The aim of this protocol is to highlight the synergistic effects of the combined use of the grinding method and application of recyclable strong solid acid nanocatalysts with inherent magnetic properties for the development of a new, ecocompatible strategy for the synthesis of azo dyes. We prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles by the co-precipitation method and subsequently coated them with tetraethoxysilane (TEOS) via a silanization process. The grafting of chlorosulfonic acid on the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs afforded sulfonic acid-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H). Therefore, we now wish to explore a convenient and green one-pot procedure for diazotization and diazo coupling reactions using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H as a proficient, mild, environmentally friendly, non-toxic and powerful magnetic nanostructure solid acid catalyst with good stability (Scheme 1). To the best of our knowledge, the use of a magnetic solid acid catalyst for the synthesis of azo

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Scheme 1 One-pot method for diazotization and diazo coupling reactions using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H under solvent-free conditions.

compounds has not been reported previously. The findings of this research may have implications for an effective synthesis on a larger scale in dyeing and medical industries (Scheme 1).

#### 2. Results and discussion

#### 2.1. Characterization of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H MNPs

The first step entails the synthesis of highly stable  $Fe_3O_4$  (**3**SiO<sub>2</sub>-SO<sub>3</sub>H MNPs. The magnetite  $Fe_3O_4$  nanoparticles were prepared using Massart's procedure<sup>19</sup> and  $Fe_3O_4$  (**3**SiO<sub>2</sub> nanocomposites were prepared according to the Stöber method.<sup>20</sup> The reaction of OH groups on  $Fe_3O_4$  (**3**SiO<sub>2</sub> with chlorosulfuric acid led to  $Fe_3O_4$  (**3**SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites (Scheme 2). The number of H<sup>+</sup> sites of magnetic solid acid was determined by pH-ISE conductivity titration (Denver Instrument Model 270) and found to be 1.25 H<sup>+</sup> sites per 1 g of solid acid at 25 °C (pH 2.30).

Fig. 1 shows the Fourier transform infrared (FTIR) pattern of the **Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H** nanocomposites. The Fe–O stretching vibration near 589 cm<sup>-1</sup> and O–H deformed vibration near 1630 cm<sup>-1</sup> were observed for the magnetic nanocomposites. The appearance of the peaks at 1195 and 1131 cm<sup>-1</sup> is ascribed to the stretching of the S–O bonds. A peak appeared at about 3320 cm<sup>-1</sup> due to the stretching of OH groups in the SO<sub>3</sub>H. On the other hand, the band in this region became much broader. All these observations confirm that the sulfonic groups have functionalized the surface of the MNPs.<sup>21</sup>

Fig. 2 presents the XRD-diffraction patterns of the Fe<sub>3</sub>O<sub>4</sub> MNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites. Fig. 2(a) shows the XRD pattern of  $Fe_3O_4$  nanoparticles, presenting the characteristic peaks of cubic structure. In Fig. 2(b), it can be seen that the diffraction peaks of Fe<sub>3</sub>O<sub>4</sub>(a)SiO<sub>2</sub> are similar to those of the parent Fe3O4 nanoparticles, which suggest that the phase structure of MNPs was well retained after forming outer  $SiO_2$  shells. Fig. 2(c) shows six characteristic peaks, which reveal a cubic iron oxide phrase  $(2\theta = 30.35, 35.95,$ 43.45, 53.70, 57.25, 62.88, 71.37, 74.46); these are related to their corresponding indices of (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (3 3 3), (4 4 0) and (5 3 1). It is implied that the resultant nanoparticles are pure Fe<sub>3</sub>O<sub>4</sub> with a spinel structure and that the grafting process did not induce any phase change of Fe<sub>3</sub>O<sub>4</sub> for the  $Fe_3O_4$  (a)  $SiO_2$ - $SO_3H$ . The weak broad band at  $2\theta$  from  $20^\circ$  to  $27^{\circ}$  in the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and the broad peaks at  $2\theta$  from  $18^{\circ}$  to  $27^{\circ}$ in the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H shown in Fig. 2(b) and (c), respectively, are ascribed to amorphous silica.22,16

The components of the  $Fe_3O_4(@SiO_2-SO_3H)$  nanocomposites were analysed, by using an energy dispersive spectrometer



Scheme 2 Preparation steps for fabricating sulfonic acid-functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles.



Fig. 1 The FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites.



Fig. 2 Powder XRD patterns: (a)  $Fe_3O_4 (c)$   $Fe_3O_4 @SiO_2$  and (c)  $Fe_3O_4 @SiO_2 - SO_3 H$  nanocomposites.



Fig. 3 The EDS of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites.

(EDS), as shown in Fig 3. The presence of S, Si, O, and Fe signals in Fig. 3 indicates that the iron oxide nanostructure has been coated by  $SO_3H$  groups.

The thermo gravimetric analysis (TGA) curves of the nano  $Fe_3O_4$  particles and  $Fe_3O_4$  (a)SiO\_2-SO\_3H nanocomposites show the mass loss of the organic materials as they decompose upon heating (Fig. 4). The initial weight loss from the magnetic nanostructures up to 126 °C is due to the removal of physically



Fig. 4 TGA curve of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4@SiO_2-SO_3H$  nanocomposites.



Fig. 5 The SEM image of (a) Fe<sub>3</sub>O<sub>4</sub> (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H before the reaction and (d) after the reaction.



Fig. 6 Magnetization curves for the  $Fe_3O_4$ ,  $Fe_3O_4$ @SiO<sub>2</sub> and  $Fe_3-O_4$ @SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites at room temperature.

adsorbed solvent and surface hydroxyl groups. The TGA curve of the  $Fe_3O_4$  (**SiO**<sub>2</sub>-**SO**<sub>3</sub>**H** was divided into several regions corresponding to different ranges of mass loss. The first region, which occurred below 160 °C, displayed a mass loss that was attributable to the loss of adsorbed solvent or trapped water from the magnetic nanocomposites. The weight loss at higher temperature (250–500 °C) could be mainly attributed to the evaporation and subsequent decomposition of SO<sub>3</sub>H moieties. The occurrence of further mass losses at higher temperature resulted from the decomposition of solica shell.<sup>23</sup>

Fig. 5 shows the SEM images of the relative magnetic nanostructures. It can be seen from Fig. 5(a) that  $Fe_3O_4$  nanoparticles have a mean diameter of about 30 nm. The SEM image shown in Fig. 5(b) demonstrates that most of  $Fe_3O_4$ @SiO<sub>2</sub>

nanocomposites are spherical with particle size of about 120 nm. Fig. 5(c) shows that  $Fe_3O_4$  (a)  $SiO_2$ - $SO_3H$  nanocomposites are nearly spherical with nano dimension ranging from 120 to 150 nm in size and have smoother surface.

The magnetic property of the nanostructures was studied by VSM, as shown in Fig. 6. The magnetization curve for  $Fe_3O_4$  nanoparticles,  $Fe_3O_4$  (**3**SiO<sub>2</sub> and  $Fe_3O_4$ (**3**SiO<sub>2</sub>-SO<sub>3</sub>H are shown in Fig. 6. The saturation magnetization of  $Fe_3O_4$ (**3**SiO<sub>2</sub> and  $Fe_3O_4$ (**3**SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites were found to be 45.87 and 22.67 emu g<sup>-1</sup>, respectively, which are much lower than that of bare  $Fe_3O_4$  (**MNPs** (67.22 emu g<sup>-1</sup>) due to the coated silica shell.

# 2.2. Diazotization and diazo coupling reactions on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H under solvent-free conditions

Diazonium salts are very important intermediates in the synthesis of organic compounds, especially azo dyes. However, the poor thermal stability of diazonium salts, strong acidic conditions, and the difficulty to separate the acidic catalysts from the reaction medium limit the application of these compounds. We tried to solve these problems by developing a green and facile procedure for the synthesis of azo dyes in the presence of a magnetic solid acid catalyst.

Initially, the efficiency of  $Fe_3O_4$  (3)  $SiO_2$ - $SO_3H$  as acidic catalyst in the diazotization reaction, followed by diazo coupling with  $\beta$ naphthol, was explored *via* a model reaction. 4-Bromoaniline was selected as a model substrate and the reaction parameters, such as amount and type of catalyst, stability of diazonium salt at room temperature, reaction time of diazotization, yield of resulted azo dyes and also reusability of solid acid catalyst, were

Entry	Catalyst (g)	Stability of diazonium salt at r.t	Time of diazotization	Yield of azo dyes (%)			
1	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H (0.2)	24 months	20 s	65			
2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H (0.4)	24 months	20 s	85			
3	$Fe_3O_4$ (0.5) <b>(0.5)</b>	24 months	20 s	90			
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H (0.6)	24 months	20 s	88			
5	$Fe_{3}O_{4}$ $O_{2}-SO_{3}H(0.7)$	24 months	20 s	82			
6	Silica phosphoric acid (0.5)	2 days	35 min	45			
7	Silica sulfonic acid (0.5)	2 days	10 min	80			
8	Silica gel (0.5)	_	No reaction				
9	$Fe_{3}O_{4}(0.5)$	_	No reaction	_			
10	$Fe_{2}O_{4}(0.5)$	_	No reaction	_			

 Table 1
 Comparison of efficiency of various catalysts for the synthesis of azo dyes

Entry	R	Time (min)	Product	Yield (%)	$MP_{rep.}/MP_{Lit.}$ (°C)
1	Н	25	2a	88	132-134/131-133 (ref. 24)
2	$2-NO_2$	30	2b	83	244-246/245 (ref. 25)
3	2-Cl	30	2 <b>c</b>	85	164-165/166 (ref. 25)
4	$4-NO_2$	25	2 <b>d</b>	90	252-254/254-256 (ref. 24)
5	4-Br	20	2e	90	157-160/157-159 (ref. 24)
6	4-Cl	20	2f	90	168-170/169-171 (ref. 24)
7	$4-CH_3CH_2$	15	2g	85	244-246/245 (ref. 25)
8	$4-CH_3$	15	2h	85	130-132/130-132 (ref. 24)
9	4-OH	10	2i	90	191-193/191-193 (ref. 26)
10	4-OMe	10	2j	92	137-138/136-137 (ref. 27)
11	4-CH <sub>3</sub> CH <sub>2</sub> O	10	2k	91	133-134/133-134 (ref. 28)
12	4-NH <sub>2</sub>	15	21	88	301-302/300-302 (ref. 29)

Table 2 The synthesis azo dyes in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H by grinding method under solvent-free conditions

examined. As shown in Table 1, the results show that  $Fe_3O_4$  (a) SiO<sub>2</sub>-SO<sub>3</sub>H nanocomposites were the best among the tested catalysts in terms of the reaction time of diazotization and synthesis of azo-dyes with excellent yields and short reaction times (Table 1, entry 3). In addition, other solid acids, such as silica phosphoric acid and silica sulfonic acid, yielded azo dyes with lower yields (Table 1, entries 6–7). Moreover, the rate of diazotization in the presence of  $Fe_3O_4$  (a)SiO<sub>2</sub>-SO<sub>3</sub>H was much higher than the other catalysts. The small size of nanoparticles and large surface to volume ratio in  $Fe_3O_4$  (a)SiO<sub>2</sub>-SO<sub>3</sub>H can be the reason for the greater stability of the diazonium salt in comparison to that supported on the bulk acid catalyst. There was no reaction in the presence of silica gel,  $Fe_3O_4$  (a)SiO<sub>2</sub> and  $Fe_3O_4$  (Table 1, entries 9–11). Interestingly, in the synthesis of azo dyes, most of the immobilized catalysts are separated by filtration; however, the magnetite-supported catalyst can be separated from the reaction system by an external permanent magnet. This will circumvent time-consuming and laborious separation steps.

After establishing the optimal conditions, in order to prove the generality of this method, different types of aromatic amine derivatives with electron-withdrawing groups as well as electron-donating groups, were converted to the corresponding azo dyes in high yields by the grinding method under solventfree conditions at room temperature (Table 2). It is important that the reaction requires a small amount of water for the formation of moist conditions and the addition of water must be carried out in a stepwise manner to ensure good yields.

The structure of azo dyes was deduced from their high-field <sup>1</sup>H NMR, IR,  $R_{\rm f}$ , and UV spectral data. Moreover, their



Fig. 7 <sup>1</sup>H NMR spectra of 1-(4-chlorophenyl azo)-2-naphthol (2f) in (a) CDCl<sub>3</sub> and (b) CDCl<sub>3</sub> + D<sub>2</sub>O.



Fig. 8 Recyclability of  $Fe_3O_4@SiO_2-SO_3H$  for the one-pot synthesis of 2e.

melting points were compared with previous reports. <sup>1</sup>H NMR spectra for compound 2f is given in Fig. 7. In the  $^{1}$ H NMR spectra in Fig 7(a), the signals of aromatic protons can be seen at  $\delta = 6$ , 88–8.56 ppm. The signal at around  $\delta = 16.11$ ppm is related to the OH proton corresponding to the N-H…O proton, which is involved in the relevant intramolecular hydrogen bond. The presence of this signal confirmed the formation of the desired products in this reaction. To prove the presence of the OH group, we have investigated the hydrogen-deuterium exchange protocol for compound 2f (Fig. 7(b)). In this method, a drop of  $D_2O$  is placed in the NMR tube containing the CDCl<sub>3</sub> solution of the compound 2f. After shaking the sample and sitting for a few minutes, the OH hydrogen is replaced by deuterium, causing it to disappear from the spectrum at  $\delta = 16.11$  ppm and a new peak appears around  $\delta = 4.89$  ppm, corresponding to DOH.

Azo dyes are usually synthesized around 0–10 °C, because temperatures above 5 °C cause the decomposition of diazonium salts and conversion to side products before coupling reactions. This is the main reason for the modest yield of the products.<sup>12</sup> To overcome this limitation, we decided to use  $Fe_3O_4$ (@SiO<sub>2</sub>-SO<sub>3</sub>H as a solid acid catalyst to be able to do the reaction at room temperature. Moreover, the stability of diazonium salts supported on solid acid nanocatalyst at room temperature significantly increased the efficiency of azo dyes synthesis.

After completion of the reaction, the separated catalyst can be reused after washing with acetone and ethanol and drying at 70 °C. We showed that the catalyst could be reused for the next cycle without great loss of catalytic activity (Fig 8). However, after 4 times of reuse,  $Fe_3O_4$ (**)**SiO<sub>2</sub>-SO<sub>3</sub>H got aggregated (as shown in SEM image Fig. 5(d)), due to which the active functional groups became unavailable. As a result, the catalyst got lost in the chemical reaction and the efficiency of recovery decreased gradually.

Titration was used to determine the acid loading of the recovered catalysts. 100 mg of recycled catalyst was stirred in 20 ml of 0.1 N NaOH solution for 30 min in an Erlenmeyer flask. The excess amount of base was then neutralized by the addition of 0.1 N HCl solution to the equivalence point of titration. The amount of *acid sites* on a solid acid surface was 1.24 H<sup>+</sup> sites per 1 g of solid acid. Thus, the magnetite solid acid catalyst is stable in the diazotization and diazo coupling reactions. This result clearly confirms that there is no leaching of SO<sub>3</sub>H groups occurring during the course of the reaction.

### 3. Conclusions

In summary, we have developed a highly efficient green method for the diazotization and subsequent azo-coupling for the preparation of azo dyes. This new protocol has some advantages over traditional methods, which include the rapid and solventfree synthesis of diazonium salts in high conversion at room temperature, long-term stability of diazonium salts supported on  $Fe_3O_4(@SiO_2-SO_3H)$ , no use of toxic solvents, acid catalysts, short reaction times in synthesis of azo compounds and recyclability of the magnetic catalyst.

### 4. Experimental

#### 4.1. Chemicals and apparatus

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively. FT-IR spectra were obtained with potassium bromide pellets in the range 400-4000 cm<sup>-1</sup> with a Perkin-Elmer 550 spectrometer. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffractometer (XRD, CuK $\alpha$ , radiation,  $\lambda = 0.154056$  nm), at a scanning speed of  $2^{\circ}$  min<sup>-1</sup> from  $10^{\circ}$  to  $100^{\circ}$  (2 $\theta$ ). Scanning electron microscopy (SEM) was performed using a FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The samples for SEM were prepared by spreading a small drop containing nanoparticles onto a silicon wafer, drying almost completely in air at room temperature for 2 h, and then transferring onto SEM conductive tapes. The transferred sample was coated with a thin layer of gold before measurement. The purity of the compounds synthesized was monitored by TLC, visualized with ultraviolet light. The known products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR data and melting point and compared with the reported values. All the yields refer to isolated products after purification.

#### 4.2. Preparation of the magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using a chemical coprecipitation method described in previous reports.<sup>30</sup> In brief, 20 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O and 10 mmol of FeCl<sub>2</sub>·4H<sub>2</sub>O were dissolved in 75 ml of distilled water in a three-necked round bottomed flask under Ar atmosphere for 30 min. Then, 10 ml of NaOH (10 M) was added into the solution within 30 min with vigorous mechanical stirring under continuous Ar atmosphere bubbling. After being rapidly stirred for 1 h, the mixture was heated to 85 °C for 1 h. The black precipitate formed was isolated by magnetic separation, exhaustively washed with double-distilled water and ethanol until neutrality and then dried at 60 °C in vacuum.

#### 4.3. Silica coated MNPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>)

The  $Fe_3O_4$  (a)  $SiO_2$  nanocomposites were prepared according to the modified Stöber method.<sup>20</sup> The details are as follows: 0.50 g

of the freshly made  $Fe_3O_4$  nanoparticles as described above were homogeneously dispersed in a mixture of 50 ml of ethanol, 9 ml of deionized water, and 1.0 ml of 28 wt% concentrated ammonia aqueous solution (NH<sub>3</sub>·3H<sub>2</sub>O), followed by the addition of 0.50 ml of TEOS. After vigorous stirring at room temperature for 16 h under Ar atmosphere, the magnetic nanocomposites (**Fe**<sub>3</sub>O<sub>4</sub>(**@SiO**<sub>2</sub>) were isolated by magnetic decantation to remove the unbounded silica particles and dried at 60 °C in vacuum after being washed with de-ionized water and ethanol.

# 4.4. General procedure for the synthesis of $Fe_3O_4$ (a)SiO<sub>2</sub>-SO<sub>3</sub>H MNPs

A 500 ml suction flask was equipped with a pressure equalizing dropping funnel, containing chlorosulfonic acid and gas inlet tube for conducting HCl gas over adsorbing the solution water. A flask was charged with  $Fe_3O_4$  (**3**SiO<sub>2</sub> nanocomposites (500 mg) and dispersed in dry  $CH_2Cl_2$  by ultrasonic bath for 30 min. Then, chlorosulfonic acid (0.4 ml in dry  $CH_2Cl_2$ ) was added dropwise manner to a cooled (ice-bath) solution of  $Fe_3O_4$  (**3**SiO<sub>2</sub> over a period of 1 h, upon which HCl gas evolved from the reaction vessel immediately. After the addition was completed, the mixture was shaken for 30 min,  $Fe_3O_4$  (**3**SiO<sub>2</sub>-SO<sub>3</sub>H was collected using a normal magnet and washed with  $CH_2Cl_2$  and methanol, before being dried in an oven at 60 °C.

## 4.5. Typical procedure for the diazotization and azo coupling reactions

4-Bromoaniline (2 mmol), Fe<sub>3</sub>O<sub>4</sub>(**3**SiO<sub>2</sub>-SO<sub>3</sub>H MNPs (0.5 g) and sodium nitrite (4 mmol, 0.276 g) were ground in a mortar with a pestle for a few minutes. Then, a few drops of water was gradually added to this and the grinding continued further for 10 min to obtain a homogeneous mixture. Then, β-naphthol (2 mmol) was added to the diazonium salt and the grinding continued for a longer time. The progress of the reaction was monitored by TLC (petroleum ether–ethyl acetate 10 : 1). The crude product was extracted with acetone (3 × 10 ml) and the solid acid was magnetically separated. The solvent was evaporated by rotary evaporator and the crude product purified by recrystallization in EtOH.

#### 4.6. Selected spectroscopic data of representative products

**Compound 2a.** Dark red needles; MP<sub>rep.</sub> (°C): 132–134; MP<sub>Lit.</sub> (°C):<sup>24</sup> 131–133; MF: C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O; MW<sub>extract</sub> (amu): 248.28; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 480 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3435 (OH), 1619 (C=C), 1457 (N=N), 1205 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.70 (d, 1H, <sup>3</sup>*J* = 9.2 Hz, Ar-H), 7.09 (t, 1H, <sup>3</sup>*J* = 7.2 Hz, Ar-H), 7.23 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.33 (m, 3H, Ar-H), 7.41 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.54 (m, 3H, Ar-H), 8.35 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H).

**Compound 2b.** Red powder; MP<sub>rep.</sub> (°C): 244–246; MP<sub>Lit.</sub> (°C):<sup>25</sup> 245; MF: C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>;  $R_f$  (in petroleum ether–ethyl acetate; 10 : 1 (v/v)): 0.13; MW<sub>extract</sub> (amu): 293.28; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 490 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3443 (OH), 1609 (C=C), 1569 (NO<sub>2</sub>), 1480 (N=N), 1315 (NO<sub>2</sub>), 1186 (C–O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.70 (d, 1H, <sup>3</sup>J = 9.5 Hz, Ar-H), 7.42

(dd, 1H,  ${}^{3}J$  = 8.3, 6.8 Hz, Ar-H), 7.50–7.56 (m, 3H, Ar-H), 7.67 (d, 1H,  ${}^{3}J$  = 9.5 Hz, Ar-H), 7.77–7.83 (dd, 1H,  ${}^{3}J$  = 8.3, 6.8 Hz, Ar-H), 8.31 (d, 1H,  ${}^{3}J$  = 8.4 Hz, Ar-H), 8.43 (d, 2H,  ${}^{3}J$  = 8.3 Hz, Ar-H), 16.75 (s, 1H, OH).

**Compound 2c.** Red powder; MP<sub>rep.</sub> (°C): 164–165; MP<sub>Lit.</sub> (°C):<sup>25</sup> 166; MF:  $C_{17}H_{12}N_2O_3$ ): MW<sub>extract</sub> (amu): 282.72; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 488 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3451 (OH), 1605 (C=C), 1500 (N=N), 1245 (C-O), 1085 (C-Cl); <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  (ppm): 7.05–7.03 (m, 4H, Ar-H), 7.44 (t, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.75 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.70 (d, 1H, <sup>3</sup>*J* = 8.4 Hz, Ar-H), 8.75 (d, 1H, <sup>3</sup>*J* = 8.4 Hz, Ar-H), 16.01 (s, 1H, OH).

**Compound 2d.** Red powder; MP<sub>rep.</sub> (°C): 252–254; MP<sub>Lit.</sub> (°C):<sup>24</sup> 254–256; MF: C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>; *R*<sub>f</sub> (in petroleum ether–ethyl acetate; 10 : 1 (v/v)): 0.28; MW<sub>extract</sub> (amu): 293.28; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 490 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3434 (OH), 1594 (C=C), 1503 (N=N), 1332 (NO<sub>2</sub>), 1201 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.81 (t, 1H, <sup>3</sup>*J* = 7.8 Hz, Ar-H), 7.43 (t, 1H, <sup>3</sup>*J* = 7.8 Ar-H), 7.59 (m, 3H, Ar-H), 7.73 (d, 1H, <sup>3</sup>*J* = 7.2 Hz, Ar-H), 7.91 (d, 1H, <sup>3</sup>*J* = 7.2 Hz, Ar-H), 8.10 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 8.51 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 16.12 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 112.33, 115.64, 117.08, 119.14, 119.52, 120.28, 121.85, 124.87, 127.20, 128.55, 130.19, 134.05, 137.46, 142.57.

**Compound 2e.** Orange red powder; MP<sub>rep.</sub> (°C): 157–160; MP<sub>Lit.</sub> (°C):<sup>24</sup> 157–159; MF: C<sub>16</sub>H<sub>11</sub>CN<sub>12</sub>O;  $R_f$  (in petroleum etherethyl acetate; 10 : 1 (v/v)): 0.47; MW<sub>extract</sub> (amu): 282.72; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 486 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3445 (OH), 1620 (C= C), 1486 (N=N), 1253 (C–O), 1090 (C–Cl); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.88 (d, 1H, <sup>3</sup>J = 9.6 Hz, Ar-H), 7.44–7.46 (m, 3H, Ar-H), 7.55 (d, 1H, <sup>3</sup>J = 7.2 Hz, Ar-H), 7.57 (d, 1H, <sup>3</sup>J = 7.2 Hz, Ar-H), 7.68–7.75 (m, 4H, Ar-H), 8.56 (d, 1H, <sup>3</sup>J = 8.1 Hz, Ar-H), 16.11 (s, 1H, OH, D<sub>2</sub>O exchangeable); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ (ppm): 115.43, 116.90, 118.45, 119.22, 120.18, 120.66, 122.88, 125.20, 128.00, 128.45, 141.22, 144.95, 147.84, 154.16.

**Compound 2f.** Bright red powder;  $MP_{rep.}$  (°C): 168–170;  $MP_{Lit.}$  (°C):<sup>24</sup> 169–171; MF:  $C_{16}H_{11}N_2OBr; R_f$  (in petroleum ether–ethyl acetate; 10 : 1 (v/v)): 0.45;  $MW_{extract}$  (amu): 327.18; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 485 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3434 (OH), 1618 (C=C), 1496 (N=N), 1142 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.88 (d, 1H, <sup>3</sup>J = 9.6 Hz, Ar-H), 7.42 (t, 1H, <sup>3</sup>J = 7.6 Hz, Ar-H), 7.55–7.61 (m, 6H, Ar-H), 8.54 (d, 1H, <sup>3</sup>J = 9.6 Hz, Ar-H), 8.56 (d, 1H, <sup>3</sup>J = 8.0 Hz, Ar-H), 16.10 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 119.92, 120.03, 120.75, 121.77, 124.55, 125.97, 128.18, 128.72, 128.99, 130.27, 132.68, 133.37, 140.36, 144.05, 171.50.

**Compound 2g.** Red powder; MP<sub>rep.</sub> (°C): 244–246; MP<sub>Lit.</sub> (°C):<sup>25</sup> 245; MF:  $C_{18}H_{16}N_2O$ ;  $R_f$  (in petroleum ether–ethyl acetate; 10 : 1 (v/v)): 0.90; MW<sub>extract</sub> (amu): 276.34; UV-Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 475 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3235 (OH), 1620 (C=C), 1504 (N=N), 11 430 (C–O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 1.43 (t, 3H, <sup>3</sup>J = 8.5 Hz, CH<sub>3</sub>), 2.52 (q, 2H, <sup>3</sup>J = 8.5 Hz, CH<sub>2</sub>), 6.83 (d, 1H, <sup>3</sup>J = 7.2 Hz, Ar-H), 6.85 (d, 1H, <sup>3</sup>J = 9.2 Hz, Ar-H), 7.20 (t, 1H, <sup>3</sup>J = 8.2 Hz, Ar-H), 7.30–7.82 (m, 5H, Ar-H), 8.58 (d, 1H, <sup>3</sup>J = 7.5 Hz, Ar-H), 16.09 (s, 1H, OH).

**Compound 2h.** Red powder;  $MP_{rep.}$  (°C): 130–132;  $MP_{Lit.}$  (°C):<sup>24</sup> 130–132; MF: C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O;  $MW_{extract}$  (amu): 262.31; UV-

Vis:  $\lambda_{max}$  CHCl<sub>3</sub> = 470 nm; IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3420 (OH), 1615 (C=C), 1500 (N=N), 1153 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 2.32 (s, 3H, CH<sub>3</sub>), 7.01 (d, 1H, <sup>3</sup>*J* = 9.2 Hz, Ar-H), 7.37 (d, 2H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.44 (t, 1H, <sup>3</sup>*J* = 7.2 Hz, Ar-H), 7.59 (t, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 7.78-7.80 (m, 3H, Ar-H), 7.82 (d, 1H, <sup>3</sup>*J* = 9.2 Hz, Ar-H), 8.57 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, Ar-H), 16.01 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 21.33, 120.12, 121.70, 123.38, 125.36, 127.82, 128.20, 129.22, 130.75, 139.10, 141.25, 144.69, 165.12.

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