



Green Synthesis of Magnetite Nanoparticles Using Brassica Napus Flower Extract: An Efficient and Highly Recyclable Catalyst for the One-pot Synthesis of Some New N, N⁻- Bis [(P-Cresol-2-Yl) Substituted Phenyl Methyl]-4, 4⁻ - Oxydianilines



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FOR the first time, magnetite (Fe₃O₄) nanoparticle was green synthesized using the extract of the Brassica napus flower-extract as a new adsorbent nanocatalyst. The characterizations have been done using XRD, UV-vis, SEM-EDX, FT-IR, and ED-XRF. As-prepared Fe₃O₄ nanoparticles were successful for the preparation of Bis-Betti bases via one-pot three component reactions of para cresol, primary diamine and substituted aromatic aldehydes to provide N, N⁻- Bis-[(p-cresol-2-yl)-substituted phenyl-methyl]-4, 4⁻ - oxydianiline derivatives. These reactions were also studied under different conditions without any catalyst by employing conventional method, ultrasonic technique and microwave irradiation. The synthesized products have been characterized by melting point, FT-IR, ¹HNMR, ¹³C NMR, Mass spectral data.

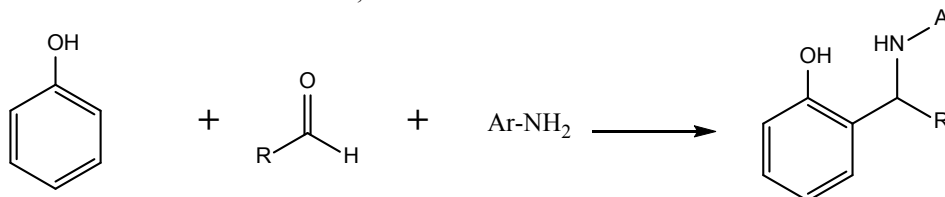
In fact, the prepared magnetite is quite effective nanocatalyst and stable for these reactions; facile, clean with high yield products. Moreover, the magnetite nanocatalyst was recovered and reused several times without considerable loss of its catalytic activity.

Keywords: Nanoparticle, Magnetite, Recyclable Catalyst, Sonication, Microwave Irradiations, Betti-base, Fe₃O₄, Brassica napus.

Introduction

At the beginning of twentieth century, simple synthesis of 1-(α -aminobenzyl)-2-naphthol from 2-naphthol, benzaldehyde and ammonia was reported by Betti [1-4]. The Betti methods can be explained of the Mannich condensation, in

which formaldehyde is substituted by an aromatic aldehyde, secondary amine by ammonia and the C-H acid by an aromatic compound that is an electronic π -rich such as 2-naphthol and phenol (Scheme 1).



Scheme 1

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The synthesis of substituted Betti base derivatives by the converted Mannich reaction then become of more importance because a C-C bond is formed under mild conditions experimentally. Utility in the chemistry of the Betti-base [5-7] has strengthened due to their attractive catalytic [8] and biological characteristic [9]. Betti base is mostly prepared by condensation of 2-naphthol, ammonia and benzaldehyde but it is thermally unsettled and thus, it is not simply to synthesize identical N, N-di-alkyl derivatives [10]. While, the alkyl derivative of Betti base has been synthesized by the main Betti methods[11].

Katritzky et al was reported most beneficial way by replacement of the benzotriazole moiety from N-[a-(dialkylamino) alkyl]benzotriazoles with phenolate anions under refluxing toluene[12]. Synthesis of a new class of Betti bases by the Mannich-type reaction: active, easy, solvent free and one pot organizer was accomplished by Aziz[13]. One-pot synthesis of new bis-Betti bases through condensation of dihydronaphthalene, aryl aldehydes and 3-amino-5-methylisoxazol has also been reported[14]. Recently, numerous modern and advance protocols have been employed to overcome the disadvantages of the traditional methods[15].

Nanoparticles, in general, are important due to their small sizes and high surface areas which enhance chemical reactivity and the rate of interactions [16, 17] and these eliminate contaminants over an extensive concentration range (~1-1000 ppm) rapidly [18]. Magnetite (Fe_3O_4) is an important member of spinel-type ferrite family, with a cubic inverse spinal structure of space group Fd_3m and an edge length of 0.839 nm [19].

This investigation for the first time employs the *Brassica napus* flower extract as a new green extract for synthesizing Fe_3O_4 -NPs as a green nanocatalyst. In fact, this study focused on the use of mentioned green-NPs catalyzed one-pot three-component synthesis of a series of new Bis-Betti-Bases.

Material And Methods

Experimental Notes

Thin Layer Chromatography was achieved by using pre-coated plate with silica gel. IR-Spectra were recorded on FT-IR spectrophotometer, 1000 (USA) Perkin Elmer (USA) as KBr disc

(Department of Chemistry, College of Science, University of Suleymani / Iraq). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra (Department of Chemistry, University of Pavia / Italy) were recorded on Ultrashield-500 plus instrument (BRUKER, Germany – 600MHz) spectrometers using DMSO & CDCl_3 as a solvent. MS instrument used in this work is ISQ Single Quadrupole MS, Germany. Gas chromatography – mass spectroscopy (GC-MS) (Department of was recorded on QP 2010 GC instrument (Shimadzu, Japan). Euro EA Elemental Analyzer 3000/Italy was used for elemental analysis (College of Education for Pure Science (Ibn al-Haitham) / Baghdad, Iraq). Melting Point were determined using Automate Melting point System Digital Image Processing Technology Stanford Research Systems.7- The Sonication was performed by Elmasonic type E 30H. The Microwave Irradiation was carried out by domestic microwave oven 900 w, 2500MHZ (Department of Chemistry, College of Science, University of Suleymani / Iraq).

Plant Material

Brassica napus is a self-compatible species exhibiting an extraordinary degree of self-pollination [20]. *Brassica napus* is a yellow flowering member of the Brassicaceae family (**Fig. 1**), also identified as the mustard or cabbage family. It is the third main source of vegetable oil in the world (behind palm oil and soybean oil) [21]. *Brassica napus* flower was collected in April 2019 from Erbil-Bastora area in the Kurdistan Region / Iraq. The plant flower was air dried under shade place at room temperature and stored in dark bottles until required.

Preparation of the *Brassica napus* flower extract

Dried flower of the plant (20.0 g) was sonicated in 200 mL double distilled water for 30 min at 60 °C. The obtained extract was filtrated then kept in a refrigerator for further steps of the study.

Synthesis of *N,N*'-Bis[(*p*-cresol-2-yl) substituted phenyl methyl] 4,4'-oxydianiline (1a-m):

Method [A]: Conventional heat.

A mixture of *p*-cresol (0.5g, 5.0mmol), 4,4'-oxydianiline (0.5g, 2.5mmol) and substituted aromatic aldehydes (5.0 mmol) in 10 ml of ethanol was heated under reflux with stirring for (22-48hr.) Completion of reaction was

indicated by TLC monitoring. The solvent was removed under reduced pressure using rotator evaporation. The reaction mixture was cooled to ambient temperature and the crude solid residue was recrystallized from ethanol to afford pure crystals of Bis Betti base (Scheme 2). The yield and melting point for all products have been summarized in table 1.

Method [B]: Ultrasonic technique [22]:

Followed the same procedure as in method [A], the mixture was sonicated instead of reflux.

Method [C]: Microwave irradiation [23, 24]:

In this method the mixture was triturated using mortar and pestle, then transferred to 50ml beaker and placed vertically in the center of domestic microwave oven which irradiated at high power (900 W) for 4-6 minutes with 20 seconds intervals. The products were crystallized in cold ethanol, filtered and dried in vacuum desiccator.

Method [D]: Green-Nanocatalyst:

Green magnetite nanocatalyst (5 g, 5 mmol) was added to a mixture of p-cresol (0.5g, 5mmol), 4,4'-oxydianiline (0.5g, 2.5mmol) and substituted aromatic aldehydes (5.0 mmol) in ethanol (10ml). The mixture was sonicated until the disappearance of the starting materials which was monitored by TLC. The crude products were filtered off and recrystallized using ethanol.

N,N'-Bis[(p-cresol-2-yl) phenyl methyl]4,4'-oxydianiline (1a):

Yellow solid; yield (0.6g, 42.5%); m.p:183.3-184.7 °C recrystallized in ethanol, $R_f=0.88$ (n-hexane: ethyl acetate) (1:4), IR (cm⁻¹): 3445 (-OH), 3250 (-NH), 3053 (Ar-H), 2878 (-CH), 1622 (C=C), 1101 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 2.0 (s, broad, 2H, NH); 8.5 (s, 2H, OH); 7-7.9 (m, 24 H, Ar-H); 5.3 (s, 2H, CH); 2.3 (s, 6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 20.0 (C_{14,14'}), 55 (C_{7,7'}), 115 (C_{2,6,2',6'}), 118.5 (C_{3,5,3',5'}), 118.9 (C_{10,10'}), 123.2 (C_{8,8'}), 126.0 (C_{18,18'}), 128.1 (C_{16,16'}), 128.3 (C_{20,20'}), 129.2 (C_{17,19,17',19'}), 130.1 (C_{11,11'}), 130.5 (C_{12,12'}), 130.8 (C_{13,13'}), 136.5 (C_{1,1'}), 144.0 (C_{15,15'}), 146.0 (C_{4,4'}), 159.6 (C_{9,9'}). Anal. calc. for C₄₀H₃₆N₂O₃: C, 81.08; H, 6.0; N, 4.72%, found: C, 81.0; H, 6.02; N, 4.54%.

N,N'-Bis[(p-cresol-2-yl) 2-hydroxy-(phenyl) methyl]4,4'-oxydianiline(1b):

White solid; yield (0.45g, 28.5%); m.p:250-252.7 °C recrystallized in ethanol, $R_f=0.66$ (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3467 (-OH), 3200 (-NH), 3042 (Ar-H), 2910 (-CH), 1619 (C=C), 1182 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 2.0 (s, broad, 2H, NH); 8.7 (s, 4H, OH); 6.9-7.5 (m, 22 H, Ar-H); 5.3 (s, 2H, CH); 2.25 (s, 6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 45.9 (C_{7,7'}), 117 (C_{2,6,2',6'}), 119.1 (C_{3,5,3',5'}), 119.2 (C_{10,10'}), 119.7 (C_{17,17'}), 122.6 (C_{8,8'}), 123.8 (C_{15,15'}), 126 (C_{19,19'}), 128.1 (C_{18,18'}), 128.3 (C_{11,11'}), 129.2 (C_{20,20'}), 130.1 (C_{12,12'}), 130.5 (C_{13,13'}), 144 (C_{1,1'}), 146 (C_{4,4'}), 156.1 (C_{9,9'}), 161.8 (C_{16,16'}). Anal. calc. for C₄₀H₃₆N₂O₅: C, 76.9; H, 5.76; N, 4.48, found: 76.0; H, 5.3; N, 4.4%.

N,N'-bis-[(p-cresol-2-yl) 3-hydroxy-(phenyl) methyl]4,4'-oxydianiline(1c):

White solid; yield (0.5g, 32%); m.p:200-204.5 °C recrystallized in ethanol, $R_f=0.625$ (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3462 (-OH), 3200 (-NH), 3036 (Ar-H), 2800 (-CH), 1627 (C=C), 1200 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 3.2 (s, broad, 2H, NH); 5.4 (s, 4H, OH); 6.5-8.0 (m, 22 H, Ar-H); 5.1 (s, 2H, CH); 2.5 (s, 6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 53.5 (C_{7,7'}), 116.0 (C_{18,18'}), 117.1 (C_{13,13'}), 118.5 (C_{16,16'}), 118.9 (C_{2,6,2',6'}), 119.0 (C_{3,5,3',5'}), 119.1 (C_{10,10'}), 121.1 (C_{8,8'}), 128.3 (C_{20,20'}), 130.1 (C_{11,11'}), 130.5 (C_{19,19'}), 132.2 (C_{12,12'}), 133.1 (C_{1,1'}), 144.0 (C_{4,4'}), 144.5 (C_{15,15'}), 156.1 (C_{9,9'}), 159.6 (C_{17,17'}). Anal. calc. for C₄₀H₃₆N₂O₅: C, 76.9; H, 5.76; N, 4.48%, found: C, 76.8; H, 5.5; N, 4.40%.

N,N'-bis-[(p-cresol-2-yl) 4-hydroxy-(phenyl) methyl]4,4'-oxydianiline(1d):

Orange solid; yield (0.6g, 40%); m.p:250-251.9 °C recrystallized in ethanol, $R_f=0.5$ (n-hexane: ethyl acetate) (1:4), IR (cm⁻¹): 3445 (-OH), 3200 (-NH), 3053 (Ar-H), 2810 (-CH), 1623 (C=C), 1163 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 8.5 (s, broad, 2H, NH); 10.1 (s, 4H, OH); 6.6-7.7 (m, 22 H, Ar-H); 3.5 (s, 2H, CH); 2.5 (s, 6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 55.9 (C_{7,7'}), 116 (C_{2,6,2',6'}), 119.1 (C_{3,5,3',5'}), 119.2 (C_{10,10'}), 119.6 (C_{8,8'}), 122.6 (C_{17,17'}), 123.8 (C_{19,19'}), 126.0 (C_{11,11'}), 128.0 (C_{16,16'}), 128.1 (C_{20,20'}),

130.1 (C_{12,12'}), 130.5 (C_{13,13'}), 132.2 (C_{15,15'}), 133.1 (C_{1,1'}), 144.0 (C_{4,4'}), 155.1 (C_{9,9'}), 161.0 (C_{18,18'}). Anal. calc. for C₄₀H₃₆N₂O₅: C, 76.9; H, 5.76; N, 4.48%, found: C, 76.0; H, 5.0; N, 4.4%.

N,N'-bis-[(*p*-cresol-2-yl)*2*-chloro- (phenyl) methyl]4,4'-oxydianiline(1e):

Light yellow solid; yield (0.4g, 40%); m.p:250-252.7 °C recrystallized in ethanol, R_f=0.66 (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3445 (-OH), 3294 (-NH), 3047 (Ar-H), 2820 (-CH), 1615 (C=C), 1254 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 3.6 (s, broad, 2H, NH); 10.5 (s, 6H, OH); 6.5-8.0 (m, 22 H, Ar-H); 5.0 (s, 2H, CH); 2.5 (6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 44.9 (C_{7,7'}), 112 (C_{2,6,2',6'}), 116.2 (C_{3,5,3',5'}), 117.1 (C_{10,10'}), 118.6 (C_{8,8'}), 127.4 (C_{19,19'}), 128.1 (C_{18,18'}), 129.2 (C_{11,11'}), 129.9 (C_{17,17'}), 130.1 (C_{20,20'}), 130.4 (C_{12,12'}), 130.5 (C_{13,13'}), 133.7 (C_{16,16'}), 144.0 (C_{1,1'}), 144.6 (C_{4,4'}), 146.0 (C_{15,15'}), 155.1 (C_{9,9'}). Anal. calc. for C₄₀H₃₄N₂O₃Cl₂: C, 72.61; H, 5.14; N, 4.23%, found: C, 72.24; H, 4.478; N, 4.88%.

N,N'-bis-[(*p*-cresol-2-yl)*3*-nitro (phenyl) methyl]4,4'-oxydianiline(1f):

Orange solid; yield (0.45, 26.5%); m.p:190-193.3 °C recrystallized in ethanol, R_f=0.33 (n-hexane: ethyl acetate) (1:4), IR (cm⁻¹): 3500 (-OH), 3200 (-NH), 3098 (Ar-H), 2800(-CH), 1626 (C=C), 1187 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 3.5 (s, broad, 2H, NH); 10.5 (s, 4H, OH); 6.39-8.4 (m, 22 H, Ar-H); 5.1 (s, 2H, CH); 2.35 (6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 53.3 (C_{7,7'}), 112 (C_{2,6,2',6'}), 116.1 (C_{3,5,3',5'}), 116.2 (C_{10,10'}), 118.1 (C_{8,8'}), 124.1 (C_{18,18'}), 128.1 (C_{16,16'}), 129.3 (C_{11,11'}), 130.1 (C_{19,19'}), 130.5 (C_{12,12',13,13'}), 130.8 (C_{20,20'}), 136.7 (C_{1,1'}), 144.5 (C_{4,4'}), 145.0 (C_{15,15'}), 145.9 (C_{17,17'}), 154.1 (C_{9,9'}). Anal. calc. for C₄₀H₃₄N₄O₇: C, 71.38; H, 4.98; N, 8.2%, found: C, 71.0; H, 4.3; N, 8.0%.

N,N'-bis-[(*p*-cresol-2-yl)*4*-dimethylamino (phenyl) methyl]4,4'-oxydianiline(1g):

Yellow solid; yield (0.5g, 31%); m.p:220-222.6 °C recrystallized in methanol, R_f=0.16 (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3500 (-OH), 3200 (-NH), 3090 (Ar-H), 2854 (-CH), 1600 (C=C), 1232 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 2.6 (s, broad, 2H, NH); 8.3 (s, 2H, OH); 6.5-8.0 (m, 22 H, Ar-H); 5.1 (s, 2H, CH);

3.0 (12H, NCH₃); 2.3 (6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 43.5 (2N(CH₃)₂), 53.3 (C_{7,7'}), 112.0 (C_{17,17',19,19'}), 113.1 (C_{2,2',6,6'}), 116.0 (C_{3,3',5,5'}), 118.0 (C_{10,10'}), 128.1 (C_{8,8'}), 129.3 (C_{11,11'}), 130.1 (C_{16,16',20,20'}), 130.4 (C_{12,12'}), 130.5 (C_{13,13'}), 130.7 (C_{15,15'}), 136.6 (C_{1,1'}), 142.5 (C_{4,4'}), 144.5 (C_{18,18'}), 154.2 (C_{9,9'}). Anal. calc. for C₄₄H₄₄N₄O₃: C, 78.10; H, 6.50; N, 8.28%, found: 78.0; H, 6.50; N, 8.08%.

N,N'-bis-[(*p*-cresol-2-yl)*3,4*-dihydroxy (phenyl) methyl]4,4'-oxydianiline(1h):

Orange solid; yield (0.1g, 6%); m.p:159-160.5 °C recrystallized in ethanol, R_f=0.65 (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3436 (-OH), 3200 (-NH), 3090 (Ar-H), 2850 (-CH), 1632 (C=C), 1165 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 4.0 (s, broad, 2H, NH); 5.0 (s, 6H, OH); 6.3-7.0 (m, 20 H, Ar-H); 5.1 (s, 2H, CH); 2.3 (6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 53.9 (C_{7,7'}), 112.0 (C_{2,2',6,6'}), 116.1 (C_{16,16'}), 117.0 (C_{3,3',5,5'}), 117.6 (C_{10,10'}), 118.1 (C_{19,19'}), 122.6 (C_{8,8'}), 128.3 (C_{20,20'}), 130.1 (C_{11,11'}), 130.5 (C_{12,12',13,13'}), 130.8 (C_{15,15'}), 136.1 (C_{1,1'}), 137 (C_{4,4'}), 142.0 (C_{18,18'}), 145.0 (C_{17,17'}), 154.2 (C_{9,9'}). Anal. calc. for C₄₀H₃₆N₂O₇: C, 73.17; H, 5.48; N, 4.26%, found: C, 73.04; H, 5.40; N, 4.0%.

N,N'-bis-[(*p*-cresol-2-yl)*2,4*-dihydroxy (phenyl) methyl]4,4'-oxydianiline(1i):

Yellow solid; yield (0.6g, 37.5%); m.p:233.3-234.7 °C recrystallized in ethanol, R_f=0.875 (n-hexane: ethyl acetate) (1:4), IR(cm⁻¹): 3435 (-OH), 3200 (-NH), 3080 (Ar-H), 2820 (-CH), 1611 (C=C), 1191 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 4.2 (s, broad, 2H, NH); 5.2 (s, 6H, OH); 6.3-7.0 (m, 20 H, Ar-H); 5.1 (s, 2H, CH); 2.5 (6H, CH₃) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = 21.0 (C_{14,14'}), 43.0 (C_{7,7'}), 103.0 (C_{17,17'}), 108.1 (C_{19,19'}), 112.0 (C_{15,15'}), 116.6 (C_{2,2',6,6'}), 118.1 (C_{3,3',5,5'}), 122.6 (C_{10,10'}), 128.3 (C_{8,8'}), 130.1 (C_{11,11'}), 130.5 (C_{20,20'}), 130.8 (C_{12,12',13,13'}), 136.1 (C_{1,1'}), 144.5 (C_{4,4'}), 154.0 (C_{9,9'}), 156.0 (C_{16,16'}), 158.2 (C_{18,18'}). Anal. calc. for C₄₀H₃₆N₂O₇: C, 73.17; H, 5.48; N, 4.26%, found: C, 73.03; H, 5.45; N, 4.22%.

N,N'-bis-[(*p*-cresol-2-yl)*4*-fluoro (phenyl) methyl]4,4'-oxydianiline(1j):

Light yellow solid; yield (0.5g, 31.5%); m.p:209.9-212 °C recrystallized in ethanol,

$R_f=0.714$ (n-hexane: ethyl acetate) (1:4), IR(cm^{-1}): 3467 (-OH), 3290 (-NH), 3070 (Ar-H), 2881 (-CH), 1625 (C=C), 1151 (C-N). $^1\text{H NMR}$ (600MHz, CDCl_3): $\delta = 2.0$ (s, broad, 2H, NH); 8.5 (s, 2H, OH); 7.0-7.9 (m, 22 H, Ar-H); 5.1 (s, 2H, CH); 2.2 (6H, CH_3) ppm. $^{13}\text{C NMR}$ (100MHz, DMSO-d_6): $\delta = 21.0$ ($\text{C}_{14,14'}$), 53.0 ($\text{C}_{7,7'}$), 115.8 ($\text{C}_{2,2',6,6'}$), 116.1 ($\text{C}_{17,17',19,19'}$), 119.4 ($\text{C}_{3,3',5,5',10,10'}$), 119.5 ($\text{C}_{8,8'}$), 122.3 ($\text{C}_{11,11'}$), 130.6 ($\text{C}_{16,16',20,20'}$), 130.7 ($\text{C}_{12,12',13,13'}$), 136.2 ($\text{C}_{15,15'}$), 140.7 ($\text{C}_{1,1'}$), 147.1 ($\text{C}_{4,4'}$), 154.2 ($\text{C}_{9,9'}$), 159.0 ($\text{C}_{18,18'}$). Anal. calc. for $\text{C}_{40}\text{H}_{34}\text{N}_2\text{O}_3\text{F}_2$: C, 76.92; H, 5.41; N, 4.48%, found: C, 76.82; H, 4.85; N, 4.40%.

N,N'-bis-[(*p*-cresol-2-yl)4-methoxy (phenyl)methyl]4,4'-oxydianiline(1k):

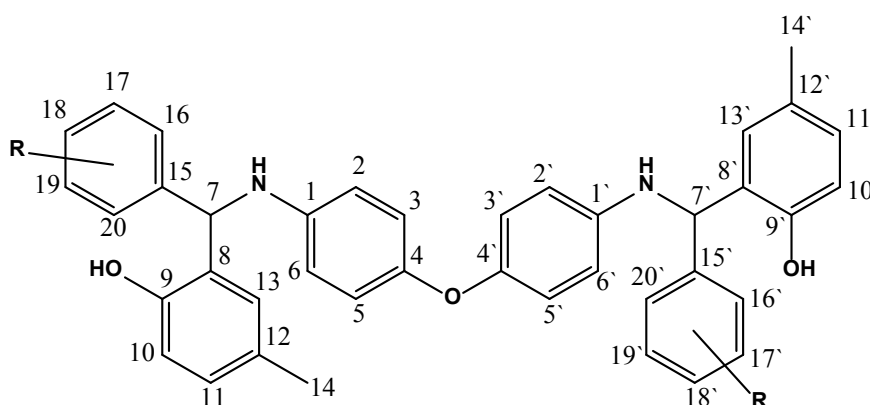
White solid; yield (0.5g, 30.5%); m.p.:236.1-238.3 °C recrystallized in ethanol, $R_f=0.83$ (n-hexane: ethyl acetate) (1:4), IR (cm^{-1}): 3459 (-OH), 3210 (-NH), 3064 (Ar-H), 2959 (-CH), 1625 (C=C), 1168(C-N). $^1\text{H NMR}$ (600MHz, CDCl_3): $\delta = 4.0$ (s, broad, 2H, NH); 10.2 (s, 2H, OH); 6.4-7.0 (m, 22 H, Ar-H); 5.1 (s, 2H, CH); 3.5 (6H, OCH_3); 3.7 (6H, CH_3) ppm. $^{13}\text{C NMR}$ (100MHz, DMSO-d_6): $\delta = 21.0$ ($\text{C}_{14,14'}$), 53.0 (OCH_3), 56.0 ($\text{C}_{7,7'}$), 112.0 ($\text{C}_{2,2',6,6'}$), 114.1 ($\text{C}_{17,17',19,19'}$), 116.0 ($\text{C}_{3,3',5,5'}$), 118.1 ($\text{C}_{10,10'}$), 128.6 ($\text{C}_{8,8'}$), 129.3 ($\text{C}_{11,11'}$), 130.1 ($\text{C}_{16,16',20,20'}$), 130.5 ($\text{C}_{12,12'}$), 130.8 ($\text{C}_{13,13'}$), 135.1 ($\text{C}_{15,15'}$), 136.0 ($\text{C}_{1,1'}$), 144.5 ($\text{C}_{4,4'}$), 154.2 ($\text{C}_{9,9'}$), 159.5 ($\text{C}_{18,18'}$). Anal. calc. for $\text{C}_{42}\text{H}_{40}\text{N}_2\text{O}_5$: C, 77.30; H, 6.13; N, 4.29%, found: C, 77.20; H, 6.1; N, 4.19%.

N,N'-bis-[(*p*-cresol-2-yl)2-hydroxy-5-methyl (phenyl)methyl]4,4'-oxydianiline(1l):

Light yellow solid; yield (0.3g, 18.75%); m.p.:250-251.5°C recrystallized in ethanol, $R_f=0.74$ (n-hexane: ethyl acetate) (1:4), IR (cm^{-1}): 3450 (-OH), 3200 (-NH), 3042 (Ar-H), 2908 (-CH), 1623 (C=C), 1251 (C-N). $^1\text{H NMR}$ (600MHz, CDCl_3): $\delta = 2.5$ (s, broad, 2H, NH); 9.2 (s, 2H, OH); 6.3-6.9 (m, 20 H, Ar-H); 5.1 (s, 2H, CH); 2.3 (12H, CH_3) ppm. $^{13}\text{C NMR}$ (100MHz, DMSO-d_6): $\delta = 21.0$ ($\text{C}_{19}\text{-CH}_3$), 21.2 ($\text{C}_{14,14'}$), 43.0 ($\text{C}_{7,7'}$), 112.0 ($\text{C}_{2,2',6,6'}$), 116.1 ($\text{C}_{3,3',5,5'}$), 118.0 ($\text{C}_{10,10',17,17'}$), 128.3 ($\text{C}_{8,8',15,15'}$), 130.1 ($\text{C}_{11,11',18,18'}$), 130.5 ($\text{C}_{12,12',19,19'}$), 130.8 ($\text{C}_{13,13',20,20'}$), 136.1 ($\text{C}_{1,1'}$), 144.5 ($\text{C}_{4,4'}$), 154.0 ($\text{C}_{9,9',16,16'}$). Anal. calc. for $\text{C}_{42}\text{H}_{40}\text{N}_2\text{O}_5$: C, 77.30; H, 6.13; N, 4.29%, found: C, 77.27; H, 6.03; N, 4.26%.

N,N'-bis-[(*p*-cresol-2-yl)4-methyl (phenyl)methyl]4,4'-oxydianiline(1m):

Light yellow solid; yield (0.1g, 12.9%); m.p.:210-211.7°C recrystallized in ethanol, $R_f=0.70$ (n-hexane: ethyl acetate) (1:4), IR (cm^{-1}): 3445 (-OH), 3200 (-NH), 3019 (Ar-H), 2912 (-CH), 1623 (C=C), 1280 (C-N). $^1\text{H NMR}$ (600MHz, CDCl_3): $\delta = 4.8$ (s, broad, 2H, NH); 10.5 (s, 2H, OH); 6.2-7.0 (m, 22 H, Ar-H); 5.1 (s, 2H, CH); 2.3 (12H, CH_3) ppm. $^{13}\text{C NMR}$ (100MHz, DMSO-d_6): $\delta = 20.9$ ($\text{C}_{18}\text{-CH}_3$), 21.0 ($\text{C}_{14,14'}$), 53.3 ($\text{C}_{7,7'}$), 112.0 ($\text{C}_{2,2',6,6'}$), 116.1 ($\text{C}_{3,3',5,5'}$), 118.0 ($\text{C}_{10,10'}$), 128.1 ($\text{C}_{8,8'}$), 128.3 ($\text{C}_{11,11'}$), 129.1 ($\text{C}_{16,16',20,20'}$), 130.4 ($\text{C}_{17,17'}$), 130.5 ($\text{C}_{12,12',13,13'}$), 130.8 ($\text{C}_{18,18'}$), 135.0 ($\text{C}_{15,15'}$), 140.0 ($\text{C}_{1,1'}$), 144.5 ($\text{C}_{4,4'}$), 154.0 ($\text{C}_{9,9'}$). Anal. calc. for $\text{C}_{42}\text{H}_{40}\text{N}_2\text{O}_3$: C, 81.29; H, 6.45; N, 4.51%, found: C, 81.09; H, 6.35; N, 4.50%.



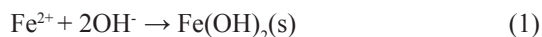
N, N'- Bis [(*p*-cresol-2-yl) substituted phenyl methyl]-4, 4' - oxydianilines

Results and Discussion

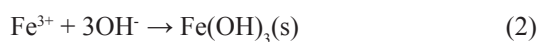
Fe₃O₄ nanoparticle formation mechanism

The mechanism of Fe₃O₄ nanoparticle formation, using FeCl₂·4H₂O, FeCl₃·6H₂O salts and Brassica napus flower extract, with continual stirring at 80 °C are given as following:

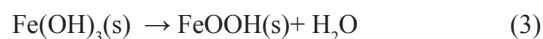
From FeCl₂·4H₂O and *Brassica napus* flower extract which is rich with brassinolide group [25].



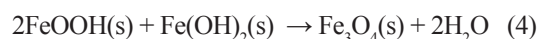
From FeCl₃·6H₂O and *Brassica napus* flower extract,



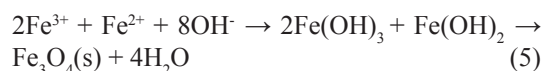
This produce,



Then from Eq. (1) and Eq. (3),



Overall this is represented by Eq. (5)



Instantaneous hydrolysis and dehydration of Fe²⁺ and Fe³⁺ salts happened throughout magnetite nanoparticle nucleation. High electron mobility between Fe²⁺ and Fe³⁺ plays an important role in crystallization process. A small proportion of Fe²⁺ ions is essential to induce crystallization of all the iron into spinal magnetite nanoparticle structures [26].

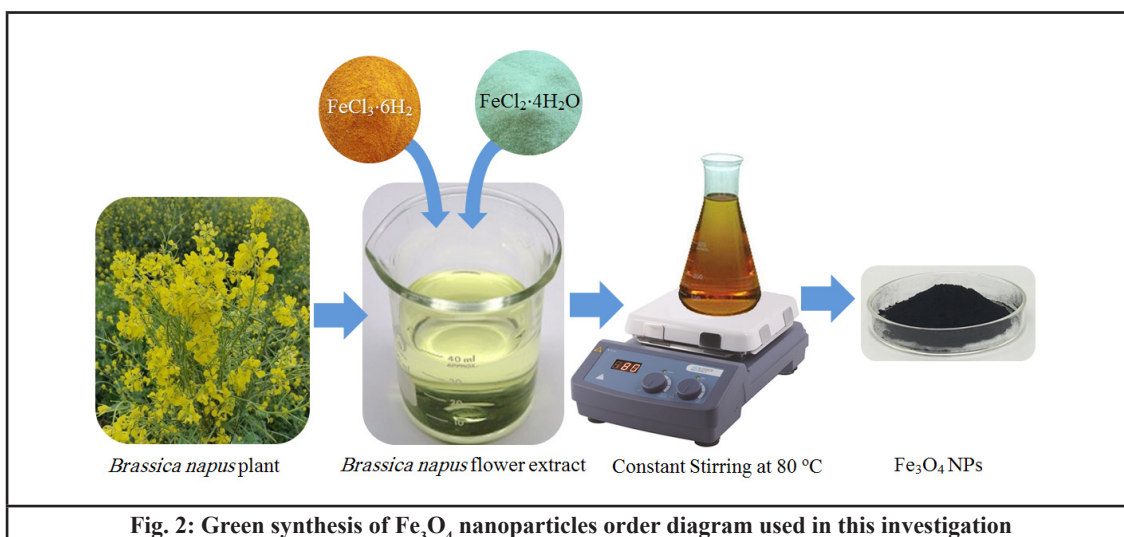


Fig. 2: Green synthesis of Fe₃O₄ nanoparticles order diagram used in this investigation

Magnetite nanoparticle characterization

Fig. 3 is a characteristic XRD pattern of the synthesized Fe₃O₄ nanoparticles. It is in an excellent agreement with the systematic procedure in JCPDS file No. 65-3107. Wide peaks specify ultra tiny and small crystallite sizes whereas sharp peaks designate an extremely crystalline nature [27]. The highest peak at 35.5° is accredited to the crystalline plane with miller indices of (311). Other characteristic peaks at 30.15° - (220), 43.18° - (400), 53.55° - (422), 57.18° - (511), 63.10° - (440), 71.49° - (533), and 74.51° - (444) (**Fig. 3**) very

close to those of the regular magnetite diffraction pattern [28]. The distinctive crystalline size of Fe₃O₄ nanoparticles is 73 nm, as expected from the dominant peak (311) diffraction peak by means of the Scherrer's equation: $D_{311} = \frac{0.94 \lambda}{\beta \cos \theta_{311}}$, where D_{311} is the typical crystalline dimension normal to the (311) crystal plane, λ is the X-ray wavelength (1.5406 Å), θ_{311} is the location of the (311) deflection peak, β is the full width at half maximum (FWHM) of the (311) plane. The nonappearance of peaks at $2\theta \approx 21^\circ$ - (110) and 33° - (104) specify the nonexistence of both goethite (α -FeOOH) and hematite (α -Fe₂O₃) in these nanoparticles [29].

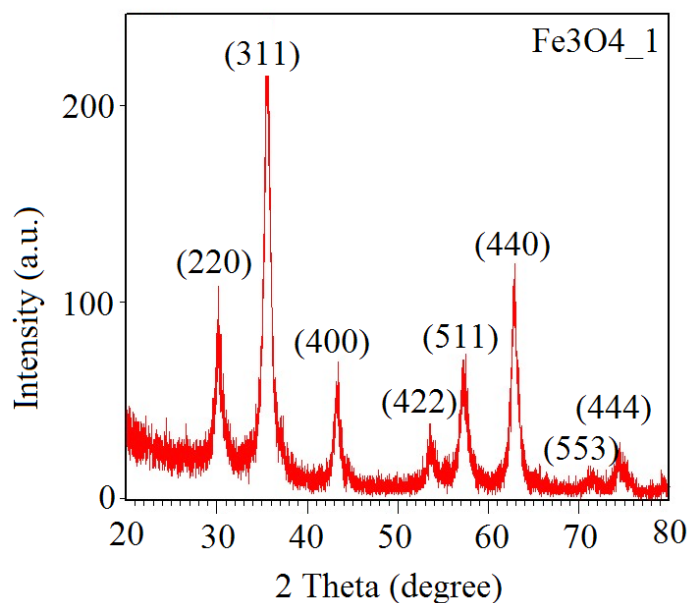


Fig 3: The powder XRD spectrum of magnetite nanoparticles

Fig. 4 shows the FT-IR spectra of as-synthesized Fe_3O_4 NPs. The bands from $574\text{--}664\text{ cm}^{-1}$ are allocated to typical Fe-O vibrations of Fe_3O_4 [30,31]. The band at 1687 cm^{-1} to bending

modes of the water molecules adsorbed on Fe_3O_4 surfaces [32]. Numerous O-H vibrations occur from $3165\text{--}3700\text{ cm}^{-1}$ [33].

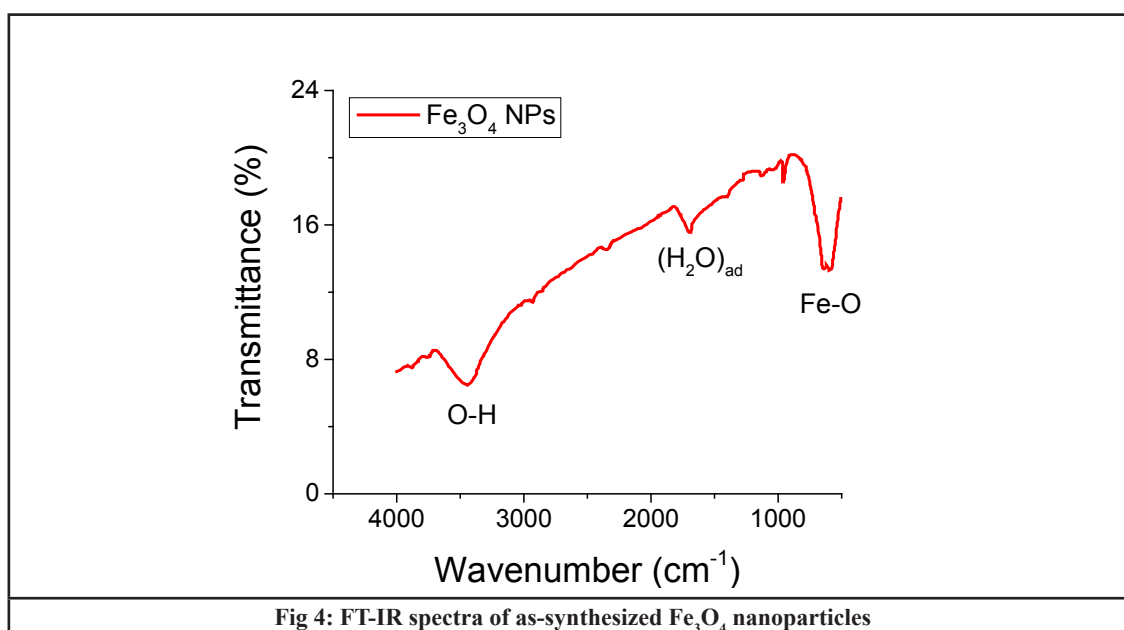


Fig 4: FT-IR spectra of as-synthesized Fe_3O_4 nanoparticles

The SEM micrographs (Fig. 5) of the prepared Fe_3O_4 nanoparticles show accumulation of these magnetic nanoparticles [34]. This accumulation

was ascribed to both magneto dipoles and Van-der Waal forces[35]. Generally, the agglomerates are in the range of a few microns.

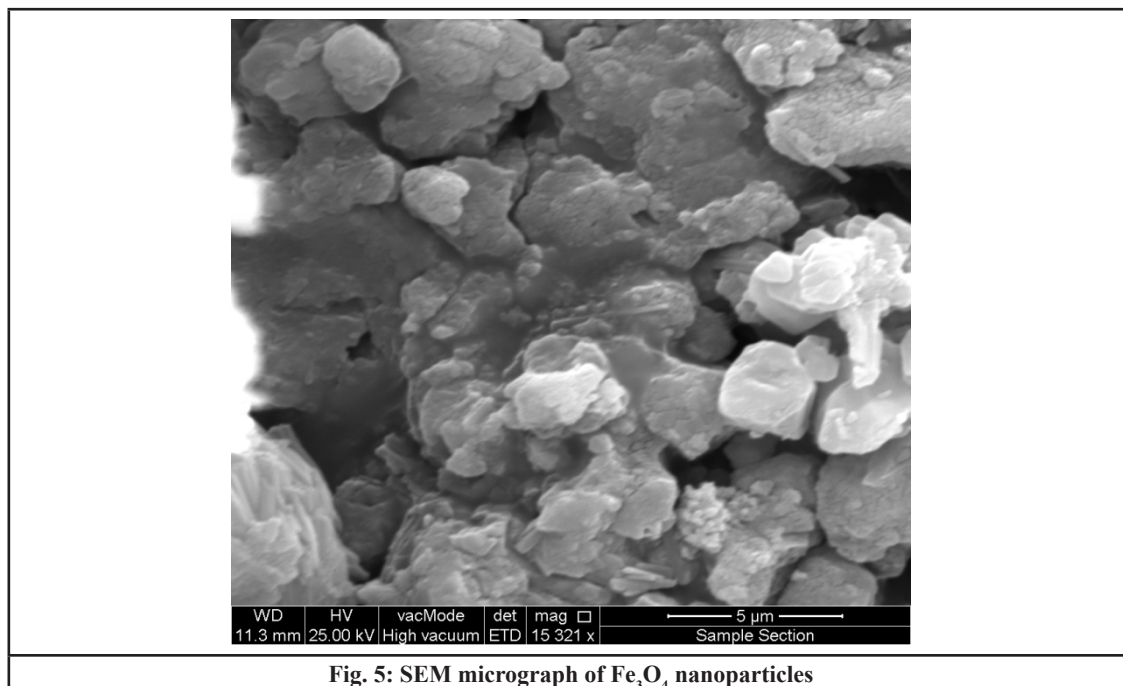


Fig. 5: SEM micrograph of Fe_3O_4 nanoparticles

The Fe_3O_4 NPs energy dispersive X-ray (EDX) configuration (**Fig. 6**) displays iron (75 %) and oxygen (17 %). Gold peaks (1.5 %) appeared

as a result of gold coating to get high quality SEM. Additional elements are appeared in minor amounts.

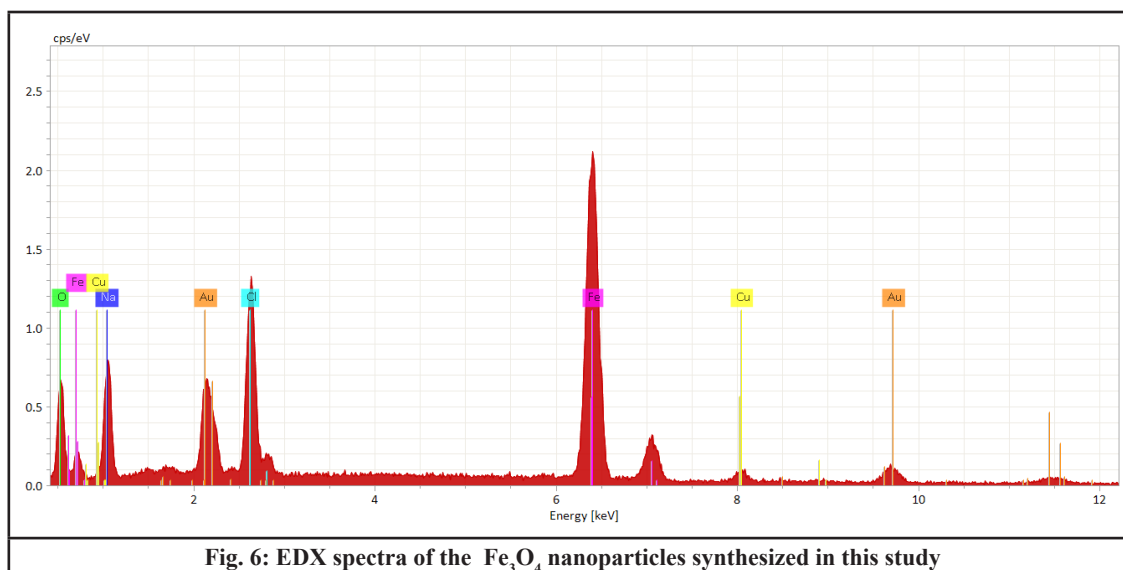


Fig. 6: EDX spectra of the Fe_3O_4 nanoparticles synthesized in this study

SEM elemental mapping obviously displays that both iron and oxygen dispersed in the Fe_3O_4 nanoparticles (**Fig. 7**). Elemental mapping

likewise confirmed that iron is the majority among the existing elements, i.e. C, O, Na, Cl, Cu and Au.

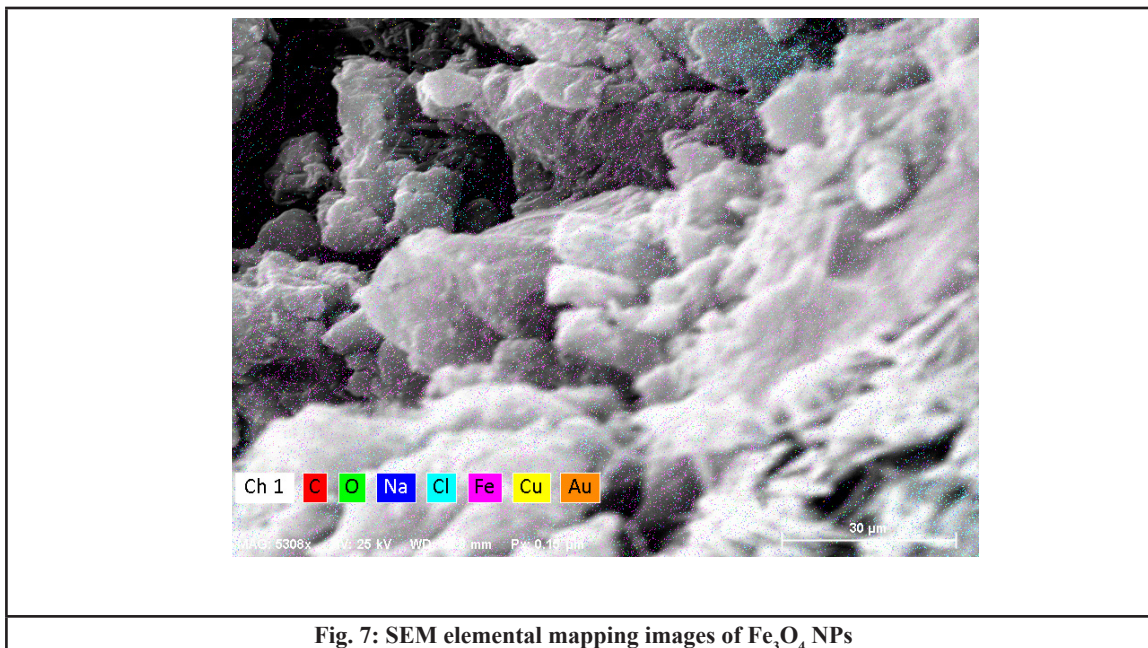
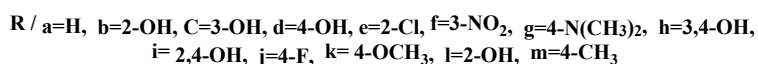
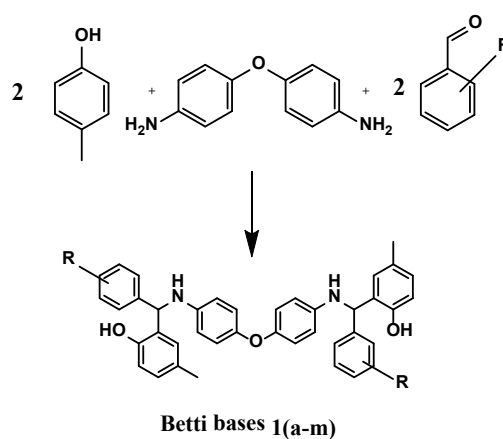


Fig. 7: SEM elemental mapping images of Fe₃O₄ NPs

Synthesis of new Bis Betti bases

Reactions between p-cresol, aromatic aldehydes and 4,4'-oxydianiline were resulted in the synthesis N,N'-Bis[(p-cresol-2-yl) substituted phenyl methyl]4,4'-oxydianiline derivatives **1a-m** (Scheme 2). These reactions were studied under four conditions, which are (1) Reflux in

ethanol (2) Ultrasound Irradiation in ethanol (3) Solvent-free microwave and (4) Green nanocatalyst. All final compounds reported in this paper are new and not found in the chemical literature and were completely characterized by spectroscopic means.



Scheme 2: Synthesis of new Bis Betti bases

The popularity of employing green NPs in organic synthesis has tremendously increased in past decade owing to the simplicity, rapidity, high turnover and green nature of the reactions. As

evident from data presented experimental section and table 1, we were able to obtain bis Betti bases (**1a-m**) in a significant high yield and shorter reaction time. The comparison of isolated yields,

reaction time and material requirements of the four conditions employed showed that green-NP method is the most efficient synthetic method in terms of amount of yields, time consumption and

the work up condition was quite easy. However, in the absence of green-catalyst, the reactions were proceeded with relatively long reaction-time (up to 48 hrs.) and very low yields.

TABLE 1: Some physical properties of N,N'-Bis[(p-cresol-2-yl) substituted phenyl methyl] 4,4'-oxydianiline 1a-m.

Compounds (I)	R	M.P. (°C)	[A] %yield	[B] %yield	[C] %yield	[D] %yield
a	H	183-185	42.5	60	40	83.3
b	2-OH	250-252	28.5	50	47	79.5
c	3-OH	202-204	32	55	50	80
d	4-OH	250-252	40	45	40	76.5
e	2-Cl	114-116	40	60	55	82
f	3-NO ₂	191-193	26.5	50	45	75
g	4-N(CH ₃) ₂	220-222	31	60	50	78
h	3,4-OH	159-161	6	5	5	50
i	2,4-OH	238-240	37.5	60	55	79.5
j	4-F	210-212	31.5	55	50	81
k	4-OCH ₃	236-238	30.5	50	40	77.5
l	2-OH	250-252	18.75	30	25	55
m	4-CH ₃	210-212	12.9	20	15	52.5

At the end of the reaction, the recyclability of the catalyst was investigated, which was recovered and reused, it has been noted there was no significant loss of efficiency. It was appeared from the results that the catalyst can be used for

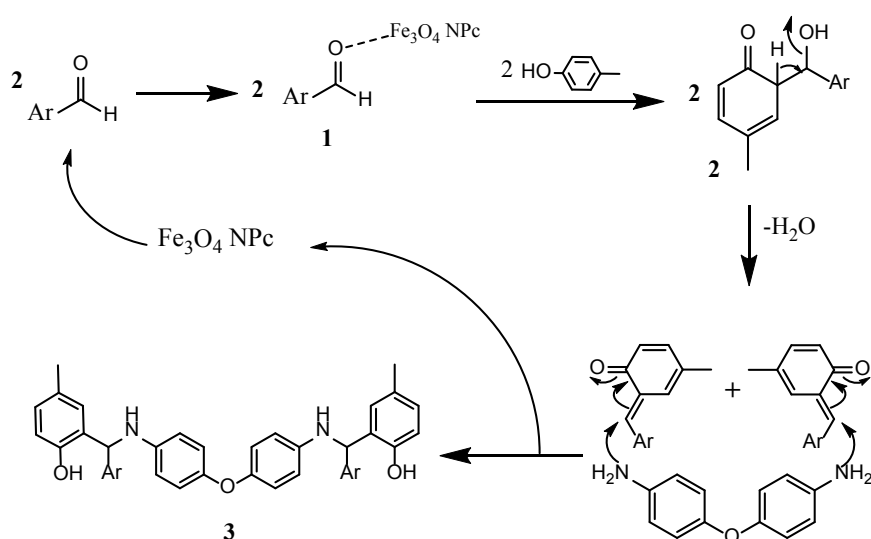
additional five times without losing its activity table 2. The structures of all the obtained products were confirmed by elemental analysis and the spectral data (FTIR, ¹HNMR, ¹³CNMR spectra.

TABLE (2) Recycling of nano-Fe₃O₄ for the preparation of functionalized P-cresol.

Run	Yield %	Run	Yield %
1	83.3	6	83.3
2	83.3	7	76
3	83.3	8	66.6
4	83.3	9	50
5	83.3	10	50

Finally, a mechanism was suggested for these reactions, which proceeds through ortho-Quinone methods [36] (Scheme 3). In the first step, NCs coordinates to aldehyde and provides the coordinated intermediate 1, which

reacts with phenol to generate the intermediate 2. Subsequently, two moles of the formed intermediate 2 reacts with one mole of di-amine to obtain the desired products 3.



Scheme (3) A suggested mechanism for synthesis of N,N'-Bis[(p-cresol-2-yl) substituted phenyl methyl]4,4'-oxydianilines

Conclusion

Fe_3O_4 nanoparticles were effectively prepared by means of a green method as a crystalline magnetite structure. XRD and SEM analysis indicated that main spherical particles were typically 70-80 nm diameters and were supplementary accumulated with inter-particle volume. Numerous analyses confirmed that Fe_3O_4 composition is dominant and the other elements present in small or trace amounts.

In this study, an efficient, simple, fast and clean condition was developed for the preparation of Bis-Betti-Bases. For the first time, biosynthesis nanostructure catalyst was prepared using the extract of the flower of *Brassica napus* which employed to the synthesis of a new series of desired compounds with high yield, short reaction time and under mild conditions without formation of any by products. The results were compared with other three methods, reflux, ultrasound-assisted, and micro-wave irradiation and found that Nano-Catalyst exhibits excellent results. Moreover, the reusability of the green catalyst for next reactions was detected.

Acknowledgement

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تخليق جسيمات المغنتيت النانوية الصديقة للبيئة باستخدام مستخلص زهرة (*Brassica napus*) : محفز فعال و قابل لإعادة التدوير لتحضير في وعاء واحد لبعض مركبات جديدة من

N, N⁻ Bis [(p-cresol-2-yl) substituted phenyl methyl]-4, 4⁻ - oxydianilines

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يتضمن البحث تخليق جسيمات المغنتيت النانوية (Fe_3O_4) الصديقة للبيئة لأول مرة باستخدام مستخلص زهرة (*Brassica napus*) كامل مساعد نانوي ، و تمت دراسة الجسيمات النانوية باستخدام XRD و Uv-Vis و SEM-EDX و FT-IR و ED-XRF . و استخدمت هذه الجسيمات النانوية لتحضير قواعد Bis-Betti من خلال تفاعلات باراكريسول و ثنائي الأمين الأولي و الديهايدات عطرية المعوضة لتكوين مشتقات :

N, N⁻ Bis [(p-cresol-2-yl) substituted phenyl methyl]-4, 4⁻ - oxydianilines

و كذلك تمت دراسة هذه التفاعلات في ظل ظروف مختلفة دون أي محفز باستخدام الطروق التقليدية و تقنية فوق الصوتية و مايكرو ويف . تم تشخيص المركبات المحضرة بواسطة الطروق الطيفية مثل طيف الأشعة تحت الحمراء (IR) و طيف الرنين النووي المغناطيسي (NMR) و طيف الكتلة (MS).

و تبينت من هذه الدراسة بان العامل المساعد النانوي المحضر فعال و مستقر و نقي و سهل الاستخدام في هذه التفاعلات و كذلك قابل لإعادة التدوير مرات عديدة دون فقدان فعاليته كعامل مساعد .