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Removal of Organic Dyes and Endocrine Disrupter by Nanocomposite of Ag(0)-Fe(0)/Fe_3O_4@GO Synthesized using a Facial Green Technique Employing *Camellia sinensis* Leaf Extract

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Abstract

The quaternary nanocomposite of Ag(0)-Fe(0)/Fe_3O_4@GO was synthesized using a facial green technique employing *Camellia sinensis* leaf extract, which acts as reducing and stabilizing agent. This nanocomposite (NC) is magnetically separable. Confirmation of the presence of total phenolic content was made by UV-visible spectroscopy. The surface deposition of Ag nanoparticles over Fe_3O_4@GO was established by the colour change to brown. The crystalline nature of green synthesized quaternary nanocomposite (Ag(0)/Fe(0)/Fe_3O_4@GO) was determined by X-ray diffraction analysis. This NC was also assessed for the catalytic behaviour under mild conditions for the removal of organic contaminants in water, i.e., Rhodamine B, Methylene blue and bisphenol A. The results revealed the excellent activity of bio-synthesized NCs within seconds. Outcomes also indicated the distinctive and combined influence of silver and iron nanoparticles on the immobilized support of Fe_3O_4@GO magnetic nanocomposite in the removal of Rhodamine B and Methylene blue. The catalyst was found more effective because of their excellent properties such as robust magnetism, easily recoverable, using an external magnet, excellent conductivity and the large surface-volume ratio. This catalyst was also found reusable and shows recyclability up to 4-5 cycles without losing its efficiency. The 70% bisphenol A removal efficiency was observed with catalyst.

***Key words*:** Quaternary nanocomposite, Green synthesis, *Camellia sinensis*, Rhodamine B, Methylene blue, BPA

The textile and printing industries are the top polluting industries in terms of volume and complexity of their effluent discharge. These industries release organic dyes exclusively, which are mutagenic as well as carcinogenic. These organic effluents cause serious damage to the underwater life leading to the destruction of aquatic beings and cause a sharp decline in photo-synthetic activity of aquatic ecosystems as well [1-5]. Mostly used organic dyes include Rhodamine B and Methylene blue. Rhodamine B is highly water soluble, cationic and carcinogenic in nature which can cause skin and eye irritation when contacted with. Similarly, Methylene blue is another cationic dye, which is widely used in bio medical sciences and long exposures to this can lead to nausea, vomiting and hypertension [2-3], [5]. Hence, Removal of these dyes is an important concern. There are many methods which are applied traditionally to treat contaminated water. These methods include incineration, precipitation, biological treatment, ozonation and adsorption on solid phase [1-2], [5]. These classical techniques have serious disadvantages like the formation of harmful by-products, extended period of treatment, foul smell, extraordinary high cost and an exhaustive energy requirement. From the last decade, the nanoparticles (NPs) are being employed extensively for decolouration, adsorption, degradation and the reduction of organic dyes [1-2], [6], [21].

In recent times, various chemical and physical methods have been utilized for synthesizing NPs of metals and their oxides, but these techniques are costly, consume more energy, and comprise harmful chemicals. Biosynthetic methods are the one among the best alternatives for their synthesis using plant extracts that are safe, green, eco-friendly and cost effective [9], [22]. On the other side, the NPs synthesized by the physical, chemical or biosynthetic methods have a common tendency of agglomeration. To prevent the agglomeration, utilization of support has attracted much attention in recent years. Support not only prevents agglomeration but also increase the efficacy and stability of the NPs. The catalysts produced by using support are heterogeneous and offer various advantages as compared to homogenous metal catalysis like easy control, hassle-free work-up, stress-free easy separation and reusability over the homogenous metal catalysis [12], [22].

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The Graphene oxide (GO) provides a promising and efficient catalytic support. Graphene oxide has a two-dimensional structure and is obtained from graphite sheets having multiple oxygen containing groups like epoxy, hydroxyl and carboxylic groups. GO is thermally and chemically stable, having a large specific surface area, good mechanical strength, better dispersion in simple solvents like water and good specific electronic conductance [22-25].

In recent times, the combination of graphene oxide and Fe_3O_4 in a single nanocomposite has become a remarkable area of the investigation [15-16]. Having an advantage of two component system, this can be used in the variety of applications. Good conductivity, robust magnetism, an enormous surface-volume ratio, and easy external magnetic recoverability are some of the exclusive properties of these type of hybrid materials [18]. Some of the green protocols have been applied for the synthesis of different nanocomposites utilizing various plant extracts and their catalytic efficiency was also investigated for the removal of different dyes and other organic effluents [15-16], [21]. As per forgoing discussion, a simple, greener, eco-friendly, and safe protocol for synthesizing Ag(0)-Fe(0)/Fe_3O_4@GO nanocomposite using *Camellia sinensis* leaf extract has been reported in this research article. The advantage of this bimetallic magnetic nanocomposite is taken to enhance the photocatalytic activity of carbon-based graphene oxide materials. Multi-metal doping has also provided a synergistic effect for visible light absorption. The Ag (0) acts as a good reducing agent, but it absorbs in the UV region due to its larger band gap. To reduce the band gap of Ag (0), it is combined with Fe (0) which absorbs in visible light. Fe (0) cannot be used alone because of its less stability and reactivity. The blend of both the metals gives a combined enhanced effect for photocatalytic dye removal [17]. The purpose of this work is to synthesize quaternary magnetic nanocomposite and to investigate its catalytic activity against the removal of Rhodamine B and Methylene blue dyes with improved recovery and reusability of the catalyst. The nanoparticles of Ag (0), Fe (0) and Fe_3O_4 are synthesized through a greener synthetic route. Further, to investigate its structure, UV- visible spectroscopy and powder XRD techniques are used. The catalytic activity of nanocomposite is evaluated for the removal of Rhodamine B, Methylene blue and BPA.

MATERIALS AND METHODS

Camellia sinensis leaves were purchased from the local market. Graphite (fine powder, extra-pure, <20 µ synthetic), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), silver nitrate ($AgNO_3$, ≥ 99.0%), potassium permanganate, hydrochloric acid, hydrogen peroxide (30% v/v), ethanol, sodium hydroxide pellets, Methylene blue and Rhodamine B were procured from Merck and Aldrich. These are used as such without any supplementary refinement. All the solutions were prepared using distilled water. Bisphenol A was provided by Sigma-Aldrich (Steinheim, Germany).

Characterization

Among the wide assortment of plants parts, green tea (*Camellia sinensis*) leaves are the frequently used plant product. These are being used in the green synthesis of Ag (0), Fe (0) and Fe_3O_4 NPs because of containing the high amount of poly-phenolic molecules (especially catechin). These molecules behave as reducing agents as well as capping agents [14]. In this study, nanocomposite is synthesized by a safe and greener method under mild reaction conditions. This eco-friendly protocol replaces hazardous chemicals by simple plant extract. The synthesized NC is not only easy to recover but its dye removal activity also doesn't decrease appreciably even after 4-5 cycle.

XRD diffraction measurements of nanocomposite were performed with analytical empyrean. Cu radiation was used to collect XRD data. UV visible spectroscopy was done on carry series UV-Visible spectrophotometer of Agilent technologies. FT-IR was done on Agilent spectrophotometer.

Preparation of Camellia sinensis leaf extract

Initially, an amount of 2 g of green tea (GT) powder was taken in 100 ml of distilled water upon continuous stirring and heating to get the GT-extract. The GT-extract was filtered, the cake was discarded and the filtrate was employed further for the preparation of nanoparticles.

Preparation of graphene oxide (GO)

The modified Hummer's method was used to prepare graphene oxide from graphite powder [20]. To prepare graphene oxide, 1.25 g of pure graphite powder was added to 0.625 ml of sodium nitrate in a round bottom flask (RBF). It was further added with 30 ml of concentrated Sulphuric acid in 10 ml portions while keeping RBF in the ice bath, being the exothermic reaction and stirred at 400 rpm for 30 minutes. Then 3.75 g of $KMnO_4$ was added slowly in 1.5 hrs. Keeping RBF in the ice bath, the solution was stirred for 40 min at 400 rpm. After 40 minutes, the flask was removed from ice bath and mixture was further stirred overnight at 400 rpm. A dark brown paste was formed. Afterwards, 60 ml of distilled water was added in 2-4 ml portions maintaining the temperature of RBF near to room temperature. The solution was stirred for 1.5 – 2 hrs. 8 ml of 30% hydrogen peroxide was added in one lot that provided effervescence and the solution was further stirred for 20 minutes. Light yellow precipitates of GO were obtained and filtered with Whatman filter paper no. 1. It was washed with 5% HCl solution and subsequently washed with distilled water until the filtrate becomes neutral to pH. The product was dried in oven overnight at 60 °C.

Synthesis of nanomaterials

Synthesis of Ag NPs

To synthesize AgNPs, silver nitrate (75 ml, 0.1 mol/L) was mixed with green tea extract (75 ml). The final solution was maintained at pH 10.5 with the addition of 1M NaOH solution. The solution was stirred for 15 min over magnetic stirrer and centrifuged for 10 minutes at 12000 rpm. The change in colour of the solution indicates the development in the synthesis of AgNPs. Supernatant was decanted off and the precipitated Ag (0) NPs were washed twice and dried in oven at 60 °C for 12 hrs [8], [10], [18].

Synthesis of Fe_3O_4 NPs

Solution of $FeSO_4.7H_2O$ (0.1 M) was prepared and a solution of NaOH (0.2 M) was added in to it drop-wise. Precipitation starts immediately. After the addition of the whole of the NaOH solution, it was kept aside for the completion of the reaction. After 30 min, the solution was separated by centrifugation twice at 3000 rpm. Supernatant was discarded. The obtained precipitates of $Fe(OH)_2$ were dissolved in 50 ml of distilled water that was further heated at water bath to boiling. The Fe_3O_4 particles start settling down upon heating. The upper clear solution was discarded. This process was repeated for 2-3 times. The precipitates were filtered using Whatman filter paper no. 1 and dried in oven at 60 °C for 3 hours. Brownish black precipitates of Fe_3O_4 were obtained which are found to be magnetic [1], [12], [19].

Synthesis of Fe (0) (nZVI)

nZVI (Nano zero valent iron) was synthesized using an eco-friendly process. Fe (0) was prepared by dissolving solid 1.39 g $FeSO_4 \cdot 7H_2O$ in 100 ml of distilled water. Further, 50 ml of GT-extract was mixed with Fe (II) solution in an inert atmosphere of nitrogen gas. After stirring for 10 minutes, the black-coloured suspension was obtained. The green tea (GT)-nZVI suspension was separated by filtration and subsequently washed with water and anhydrous ethanol. The GT-nZVI was dried overnight in an oven at 60°C [9].

Synthesis of Fe_3O_4@ GO

The synthesized Fe_3O_4 NPs were added to the 0.1% suspension of GO in distilled water and the mixture was sonicated for 15 minutes. Then this suspension was filtered and dried in oven at 80 °C for 4 hours [6], [13], [16].

Synthesis of Ag (0)-Fe (0)/Fe_3O_4@GO nanocomposite (NC)

0.3 g of Fe_3O_4@GO nano-composite was dissolved in 30 ml water by sonicating for 15 minutes. Further, 15 ml of an aqueous solution of $AgNO_3$ (0.1 M) and 15 ml of $FeSO_4.7H_2O$ (0.5 M) was mixed slowly into the suspension of Fe_3O_4@GO nanocomposite. Subsequently, it was sonicated for 1 hr and 40 ml of aqueous *Camellia sinensis* leaf extract (5.0 g/L) was added slowly into it. pH of the solution was maintained at 9.0 using an aqueous solution of sodium hydroxide with constant stirring and heating (under reflux) for 24 hours at 80 °C. Upon completion, the Ag-Fe/Fe_3O_4@GO nanocomposite was isolated by using an external magnet. NC was washed multiple times with water and dried overnight in an oven at 60 °C for its use.

RESULTS AND DISCUSSION

Identification of NC

UV-Visible spectroscopy

The UV–Visible spectrum of *Camellia sinensis* leaf extract presented the bands at 300 nm and 369 nm corresponding to $\pi \rightarrow \pi^*$ transitions of phenolic aromatic systems of the extract. These bands are due to localized transitions within the benzoyl ring and cinnamoyl ring systems. The UV-Visible spectrum of Ag NPs synthesized using *Camellia sinensis* leaf extract. This presented a broad peak at 460 nm, representing the surface plasmon response (SPR) of Ag NPs in solution [2].

XRD patterns

(Fig 1) shows the XRD pattern of Ag(0)-Fe(0)/Fe_3O_4@GO nanocomposite. The XRD peaks of this nanocomposite have been marked at an angle 2Θ=39.04° (111), 2Θ=45.26° (200), 2Θ=65.4° (220), and 2Θ=78.3° (311). All these peaks have been matched with JCPDS file for Ag (JCPDS 04-0783), for Fe_2O_3 (JCPDS 001-136), for Fe_3O_4 (JCPDS 002-1035) and for Fe (0) (JCPDS 06-696), which confirm the crystalline structure of nanocomposite.

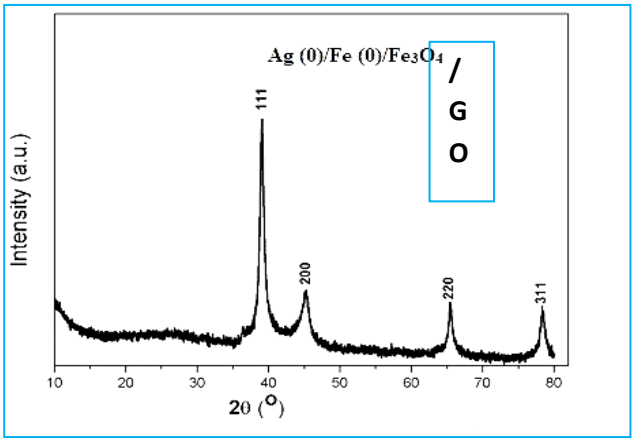

Fig 1 XRD pattern of Ag (0)-Fe (0)/Fe_3O_4@GO NC

EDX spectra

To confirm the elemental composition of Ag (0)-Fe (0)/Fe_3O_4@GO, NC was analyzed by EDX analysis. This analysis confirmed the presence of oxygen (O), carbon (C), iron (Fe) and silver (Ag) in 30.36%, 29.12%, 27.87% and 12.67% by weight respectively in Ag (0)-Fe (0)/Fe_3O_4@GO NC.

SEM images

The morphology of the surface of Ag (0)-Fe (0)/Fe_3O_4@GO is analyzed using SEM technique. The images are demonstrated in (Fig 2a-b). Images show spherical particles. The GO surface is covered by Ag, Fe and Fe_3O_4.

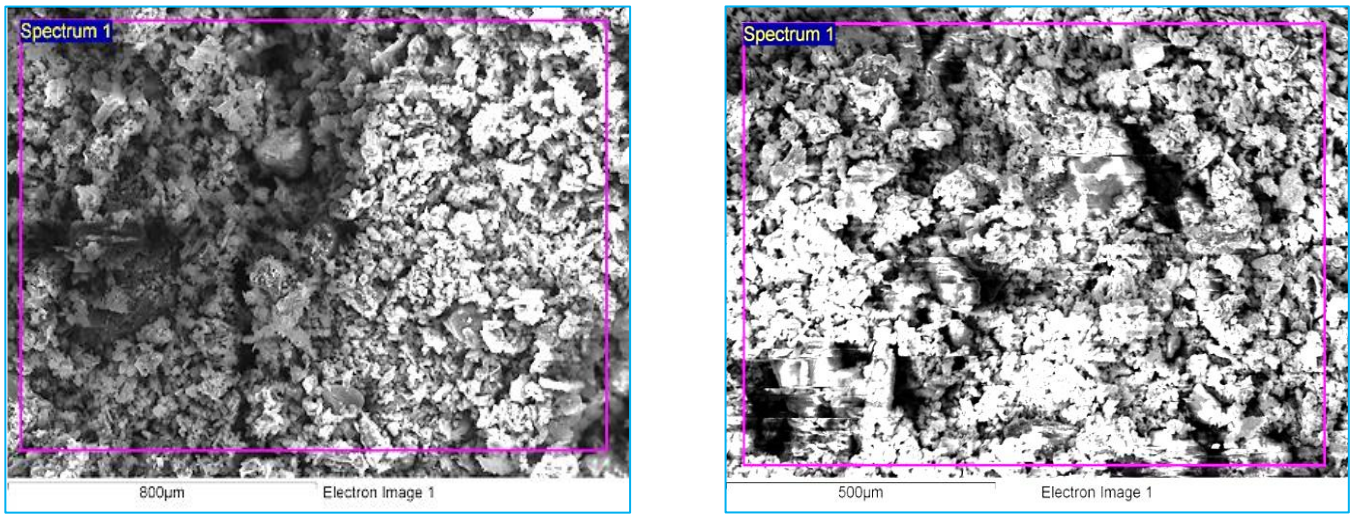

Fig 2 (a) and (b) SEM images of quaternary magnetic nanocomposite (NC)

Raman spectra

This technique is used to characterize carbon supported material having alternative double bonds. The Raman spectra of graphene oxide exhibited two fundamental vibrations at 1319 and 1605 cm^{-1} correspond to the D and G bands respectively. The D and G bands at 1300 and 1600 cm^{-1} shows the shifting of D and G band in NC that are due to strong interaction between AgNPs, FeNPs and GO.

The catalytic action of quaternary magnetic nanocomposite for the removal of dyes and endocrine disrupters from water

Removal of rhodamine B

After determining the structure of nanocomposite, its catalytic action was investigated for the removal of organic dye, i.e., Rhodamine B. This dye is one of the highly poisonous organic contaminants and its removal under normal conditions is quite challenging. It is very tough to remove the dye without using the catalyst due to kinetic barrier [2-3], [5], [7]. The catalytic removal of Rhodamine B was performed at room temperature in aqueous medium and was observed by visualizing UV-visible spectra as a function of time. The Rhodamine B has absorption maxima at 553 nm in aqueous medium. After the addition of 40 mg of NC to 10 ml aqueous solution of dye, it was stirred at 220 rpm using a magnetic stirrer. The time taken by dye to decolourise the solution was noted.

Comparison of catalytic activity of NC and its constituent in the removal of Rhodamine B

The comparative dye removal by nanocomposite and its constituents is shown in (Fig 3). It is clearly shown that the dye is removed by GO, Ag(0) and NC which is indicated by the disappearance of the absorption peak of Rhodamine B at 540-580 nm.

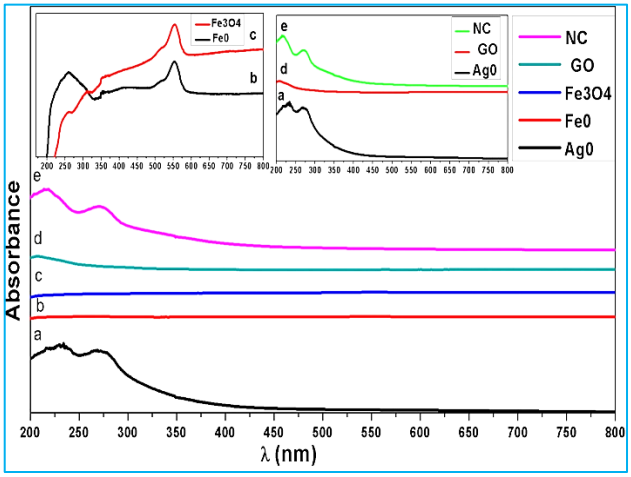

Fig 3 UV-Visible spectral analysis for the catalytic removal of rhodamine B under different conditions: (a) Ag(0) (b) Fe(0) (c) Fe_3O_4 (d) GO (e) NC

Efficacy of the NC in the removal of Rhodamine B

The time taken by the different components individually as well as NC to remove Rhodamine B from aqueous solution was investigated. It shows the high efficacy of NC in the removal of Rhodamine B. The catalyst Ag(0), GO and NC took time of 240s, 120s and 55s respectively.

Recyclability of NC in the removal of Rhodamine B

40 mg of NC was taken to 10 ml of aqueous solution of Rhodamine B. Upon completion, the NC was recovered magnetically using an external magnet. Later, it was washed and dried. The NC was reused for 4-5 times and time taken to remove the dye was noted. The results showed the reusability of the NC up to 5 cycles in good catalytic activity.

Removal of Methylene blue

Catalytic removal of Methylene blue was performed under normal conditions in aqueous medium and observed using UV-Visible spectra as a function of time. The methylene blue has λ_{max} at 663 nm in aqueous medium. After the addition of catalyst to an aqueous solution of dye, it was stirred at magnetic stirrer under normal conditions. The time taken by nano catalyst to decolourise the solution was noted.

Comparison of catalytic activity of NC and its constituents in the removal of Methylene blue dye

Figure 4 presents the comparative analysis of dye removal by nanocomposite and its constituents. It is clearly shown that the dye is removed by GO, Ag (0) an NC as indicated by the disappearance of absorption peak of Methylene blue at 663 nm.

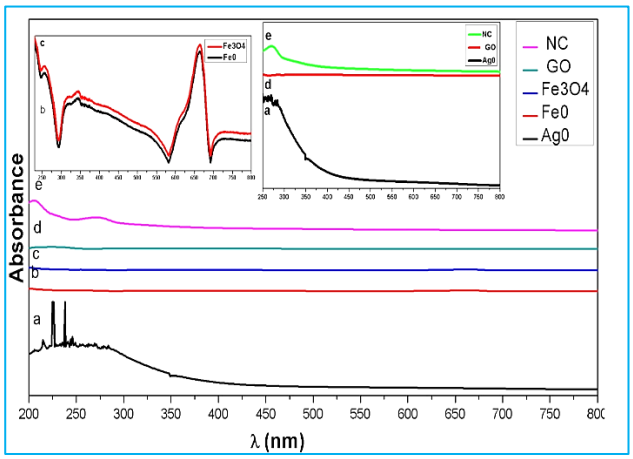

Fig 4 UV-Visible spectra of catalytic removal of Methylene blue: (a) Ag (0) (b) Fe (0) (c) Fe_3O_4 (d) GO (e) NC

Efficacy of the NC

The time taken by the different components individually as well as NC to remove methylene blue from aqueous solution was analyzed. The NC has shown high efficacy in removing methylene blue. The catalyst Ag(0), GO and NC took time of 300s, 360s and130s respectively.

Recyclability of NC in the removal of Methylene blue

40 mg of NC was added to 10 ml of aqueous solution of Methylene blue. Upon completion, the NC was recovered magnetically, afterward washed and dried. The NC was reused for 4-5 times and time taken to remove the dye was noted. The results presented the reusability of NC catalyst up to 5 cycles with good catalytic activity.

Removal of bisphenol A.

A 5 mg/L solution of bisphenol A (BPA) was made in methanol. After the addition of catalyst to an aqueous solution of BPA, it was stirred at magnetic stirrer under normal conditions The determination of bisphenol A in sample was performed using microextraction in packed syringe and gas chromatography–mass spectrometry methods previously developed in our lab [26]. The total 70% of BPA adsorption was observed.

CONCLUSION

The magnetic nanocomposite was synthesized by a facile, efficient; eco-friendly and green route using green tea (*Camellia sinensis*) leaves as reducing and stabilizing agent. The nanocomposite is synthesized using mild reaction conditions. The reported method is safe, cost effective and free from toxic and hazardous chemicals. This catalyst was successfully evaluated for the removal of Rhodamine B and Methylene blue. The catalyst was recovered easily by using an external magnet and found to be effective for its reuse up-to 4-

5 cycles without any considerable decrease of catalytic activity. This green synthesized quaternary NC was found to be extremely effective for removal of organic dyes and BPA.

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LITERATURE CITED

1. Kristianto Y, Saleh R. 2018. Facile synthesis of $Ag/Fe_3O_4/ZrO_2$ composites coupled with nanographene platelets for photo-and sonophotocatalytic activities against methylene blue dye, In: AIP Conference Proceedings, Vol 2023. (Eds) Mart T, Triyono D, Anggraningrum IT, Sugeng KA, and Yuniati R. AIP Publishing LLC. pp 020014.
2. Adyani SH, Soleimani E. 2019. Green synthesis of Ag/Fe_3O_4/RGO nanocomposites by *Punica Granatum* peel extract: Catalytic activity for reduction of organic pollutants. *Int. Jr. Hydrog. Energy* 44(5): 2711-2730.
3. Martínez-Huitle CA, Brillas E. 2009. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. *Appl. Catal. B. Environ*. 87(3/4):105-145.
4. Wu Q, Feng C, Wang C, Wang Z. 2013. A facile one-pot solvothermal method to produce superparamagnetic graphene–Fe_3O_4 nanocomposite and its application in the removal of dye from aqueous solution. *Colloids Surf. B: Biointerfaces* 101: 210-214.
5. Banat IM, Nigam P, Singh D, Marchant R. 1996. Microbial decolorization of textile-dyecontaining effluents: a review. *Bioresource Technology* 58(3): 217-227.
6. Atarod M, Nasrollahzadeh M, Sajadi SM. 2015. Green synthesis of a Cu/reduced graphene oxide/Fe_3O_4 nanocomposite using *Euphorbia wallichii* leaf extract and its application as a recyclable and heterogeneous catalyst for the reduction of 4-nitrophenol and rhodamine B. *RSC Adv*. 5(111): 91532-91543.
7. Atarod M, Nasrollahzadeh M, Sajadi SM. 2016. Green synthesis of Pd/RGO/Fe_3O_4 nanocomposite using *Withania coagulans* leaf extract and its application as magnetically separable and reusable catalyst for the reduction of 4-nitrophenol. *Jr. Colloid Interface Science* 465: 249-258.
8. Han Y, Luo Z, Yuwen L, Tian J, Zhu X, Wang L. 2013. Synthesis of silver nanoparticles on reduced graphene oxide under microwave irradiation with starch as an ideal reductant and stabilizer. *Appl. Surf. Science* 266: 188-193.
9. Hoag GE, Collins JB, Holcomb JL, Hoag JR, Nadagouda MN, Varma RS. 2009. Degradation of bromothymol blue by 'greener'nano-scale zero-valent iron synthesized using tea polyphenols. *Mater. Chem*. 19(45): 8671-8677.
10. Junejo Y, Baykal A, Safdar M, Balouch A. 2014. A novel green synthesis and characterization of Ag-NPs with its ultra-rapid catalytic reduction of methyl green dye. *Appl. Surf. Science* 290: 499-503.
11. Kumar S, Nair RR, Pillai PB, Gupta SN, Iyengar M, Sood A. 2014. Graphene oxide–$MnFe_2O_4$ magnetic nanohybrids for efficient removal of lead and arsenic from water. *ACS Appl. Mater. Interfaces* 6(20): 17426-17436.
12. Nasrollahzadeh M, Atarod M, Sajadi SM. 2016. Green synthesis of the Cu/Fe_3O_4 nanoparticles using *Morinda morindoides* leaf aqueous extract: a highly efficient magnetically separable catalyst for the reduction of organic dyes in aqueous medium at room temperature. *Appl. Surf. Science* 364: 636-644.
13. Nasrollahzadeh M, Azarian A, Ehsani A, Sajadi SM, Babaei F. 2014. Hybrid Pd/Fe_3O_4 nanowires: Fabrication, characterization, optical properties and application as magnetically reusable catalyst for the synthesis of N-monosubstituted ureas under ligand-free conditions. *Mater. Res. Bulletin* 55: 168-175.
14. Rolim WR, Pelegrino MT, de Araújo Lima B. 2019. Green tea extract mediated biogenic synthesis of silver nanoparticles: Characterization, cytotoxicity evaluation and antibacterial activity. *Appl. Surf. Scienec* 463: 66-74.
15. Thu TV, Ko PJ, Nguyen TV. 2017. Green synthesis of reduced graphene oxide/Fe_3O_4/Ag ternary nanohybrid and its application as magnetically recoverable catalyst in the reduction of 4-nitrophenol. *Appl. Organomet. Chem*. 31(11): e3781.
16. Vinothkannan M, Karthikeyan C, Kim AR, Yoo DJ. 2015. One-pot green synthesis of reduced graphene oxide (RGO)/Fe_3O_4 nanocomposites and its catalytic activity toward methylene blue dye degradation. *Spectrochim. Acta A: Mol. Biomol. Spectrosc*. 136: 256-264.
17. Zhao Z, Cai Z, Yang L. 2018. Ternary magnetic Ag–Cu/Fe_3O_4/RGO composite as an efficient photocatalyst for degradation of malachite green. *Jr. Mater. Sci.: Mater. Electron* 29(20): 17743-17749.
18. Pai S, Kini MS, Selvaraj R. 2021. A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites. Environ. *Sci. Pollut. Research* 28: 11835-11849.
19. Sarojini G, Kannan P, Rajamohan N, Rajasimman M, Vo DVN. 2023. Dyes removal from water using polymeric nanocomposites: A review. *Environ. Chem. Letters* 21(2): 1029-1058.
20. Umejuru EC, Mashifana T, Kandjou V. 2023. Application of zeolite-based nanocomposites for wastewater remediation: Evaluating newer and environmentally benign approaches. *Environ. Research* 231: 116073.
21. Mehdizadeh A, Najafi Moghadam P, Ehsanimehr S, Fareghi AR. 2022. Preparation of a new magnetic nanocomposite for the removal of dye pollutions from aqueous solutions: synthesis and characterization. *Mater. Chem. Horiz*. 1(1): 23-34.
22. Nasrollahzadeh M, Maham M, Rostami-Vartooni A, Bagherzadeh M, Sajadi SM. 2015. Barberry fruit extract assisted in situ green synthesis of Cu nanoparticles supported on a reduced graphene oxide–Fe_3O_4 nanocomposite as a magnetically separable and reusable catalyst for the O-arylation of phenols with aryl halides under ligand-free conditions. *RSC Adv*. 5(79): 64769-64780.
23. Dreyer DR, Park S, Bielawski CW, Ruoff RS. 2010. The chemistry of graphene oxide. *Chem. Soc. Rev*. 39(1): 228-240.
24. Jo J, Lee S, Gim J, Song J. 2019. Facile synthesis of reduced graphene oxide by modified Hummer's method as anode material for Li-, Na-and K-ion secondary batteries. *R. Soc. Open Science* 6(4): 181978.
25. Senthilvelan S, Chandraboss V, Karthikeyan B, Natanapatham L, Murugavelu M. 2013. TiO_2, ZnO and nanobimetallic silica catalyzed photodegradation of methyl green. *Mater. Sci. Semicond. Process* 16(1): 185-192.
26. Kumar A, Singh D, Bhandari R, Malik AK, Kaur S, Singh B. 2023. Bisphenol A in canned soft drinks, plastic-bottled water, and household water tank from Punjab, India. *Jr. Hazard. Mater* 9: 100205.