Journal of Applied Research in Science and Humanities

Towards green and sustainable environment future: Harnessing natural sources to synthesize catalysts for promising applications

Yasmine Islam Nasser –Yasmine Ramadan Hussein–Yasmine Magde –Youmna Emad salah– Youmna yasser Hassan–Youstina Hany Alfy_Youstina Ayman Roshdy

Supervisor: Marwa M. Ibrahim, Assistant Professor, Physical Chemistry

Ain Shams University, Faculty of Education, Program: Science

Abstract

In order to have a sustainable and a clean environment, green chemistry is crucial in today's society. The creation and improvement of iron oxide nanocatalysts for the effective reduction of organic dyes in aqueous solutions is presented in this study. The iron oxide nanocatalysts were prepared using clove and green coffee extract and characterized using advanced techniques such as XRD. The XRD analysis shows the formation of hematite and magnetite forms of iron oxide after calcination at 550 °C. The samples which prepared without calcination have amorphous structures. By producing hydrogen from $NaBH_4$, which was utilized in the reduction of organic dyes (Methylene blue and Remazol red), the sample's catalytic activities were assessed. The results confirmed that iron oxide which prepared using green coffee extract and calcined at 550 °C has the highest reduction activity compared with the other studied catalysts according to its small crystal size and high surface area. Also, the iron oxide has good stability and durability after multiple runs for reduction of remazole red dye.

Key Words:

Green synthesis, Fe_2O_3 , catalysts, $NaBH_4$ hydrolysis, dye reduction

1. Introduction:

As cities and industries expand, pollution is regarded as a serious issue that is becoming more and more of a concern. Numerous waterways in the world are contaminated by industrial and municipal trash. Urban regions can have

high levels of air pollution. The landfills lack suitable development and management. Pollution is now a health hazard for both humans and animals (Bruce et al., 2000, 1078–1092). So, the definition of pollution is the presence of a substance in the environment that because of its chemical composition or quantity inhibits the functioning of natural processes and generates adverse environmental and health effects (Mohamed et al., 2023, 7227). It can be categorized according on its physical characteristics, source, recipient, or effects. Thus, pollution might be classified as physical, economic, political, social, or religious. There are ten primary common categories of pollution are presented like air, water, land, noise, heat, radiation, light, urban, plastic, and radioactive materials (Sadiku et al., 2020, 155–161). The water pollution is examined here.

The poisoning of water, including lakes, rivers, streams, seas, and so forth. Pollutants have been introduced into water bodies, causing environmental damage. It degrades the water's purity and renders it unfit for human consumption. Waterborne illnesses like giardiasis, hookworm, typhoid, and liver and kidney damage are brought on by contaminated drinking water. For instance, too much nitrate in drinking water is bad for human health and newborns. Human activity is mostly to blame for water contamination, which frequently arises from poor waste management techniques, industrial operations, agricultural practices, and urbanization. Numerous pollutants, including heavy metals, hazardous chemicals, organic compounds, dyes, and other industrial wastes, are discharged into water bodies by industries. Wastewater from urban areas is produced in large quantities and contains chemicals, detergents, human waste, and other pollutants. One of the main causes of water contamination is agriculture. Overuse of pesticides, herbicides, and fertilizers can cause these chemicals to leak into adjacent streams. Agriculturally produced nutrients such as phosphorus and nitrogen can result in eutrophication, which lowers oxygen levels and damages aquatic ecosystems (Tzanakakis et al., 2020, 2347) (Ighalo et al., 2021, 124566) (Valatin et al., 2022, 101373). Fig. 1 shows the example of water pollution.

Figure (1): the example of water pollution.

The majority of dyes are created during the production of textiles, printing, and paper (Al-tQahani et al., 2022, 1822–1833) and they are also utilized in a variety of industries, including the pharmaceutical and cosmetics industries (Priyadharsini et al.,

2023, 139180). Despite the fact that these dyes have many advantageous industrial applications (Naseem et al., 2024, 124450). Industries that release wastewater containing these dyes into aquatic habitats cause a number of environmental issues, including reduced sunlight dispersion, increased chemical and biological oxygen demands, restricted photosynthesis, and delayed plant growth. Dyes are not only carcinogenic, mutagenic, poisonous, and bioaccumulative, but they are also extremely difficult to remove (Priyadharsini et al., 2023, 139180). Because of these negative effects, industrial effluent must have its colors removed before being released into water streams (Naseem et al., 2024, 124450). For wastewater containing dyes to be properly detoxified, cost–effective and ecologically friendly treatment methods must be developed immediately. Numerous techniques, including as adsorption, ion exchange, extraction, and catalytic reduction, have been documented for the removal of these dyes. The use of the catalytic reduction approach to restore harmful chemicals to the environment has received a lot of attention recently. Reducing dyes is therefore essential since it may lead to fewer toxic compounds and a lower risk of health issues (Din et al., 2024, 100002).

Hydrogen can be produced and stored in a variety of physical and chemical ways. Chemical metal hydrides, for instance. Like sodium borohydride, potassium borohydride, and lithium borohydride. The alkali (Li, Na, and K) borohydrides (MBH_4) have a great ability to produce and store hydrogen (Retnamma et al., 2011, 9772–9790) (Rusman et al., 2016, 12108–12126). Because of its significant benefits, including its capacity to produce hydrogen in a controlled manner and store a large amount of hydrogen, $NaBH_4$ is the most commonly employed of all the hydrides (Ekınc, 2020, 589–594). Additionally, the mass of hydrogen produced by the hydrolysis of sodium borohydride is 10.8% (Fakioğlu et al., 2004, 1371–1376). The hydrolysis of NaBH4 is presented by the following equation (Salman et al., 2022, 2200433):

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (\Delta H^0 = -214\ \text{kJ/mol})$$

According to reports, when $NaBH_4$ is hydrolyzed at room temperature without catalysts, the rate at which hydrogen is produced is incredibly low. This is due to the fact that at lower temperatures, the activation energy reaction is greater (Prasad et al., 2019, 538–551) (Patil et al., 2021, 130988). Thus, an efficient catalyst is required to promote and accelerate the self–hydrolysis of the $NaBH_4$ process (Retnamma et al., 2011, 9772–9790). Building cheaper, more effective catalysts has been essential in recent years for high–performance, realistic H_2 production (Friend et al., 2017, 517).

The catalysts in the $NaBH_4$ hydrolysis reaction showed excellent catalytic activity for H_2 evolution. Transition metal oxides are currently often used for the hydrolysis of $NaBH_4$ because of their inexpensive cost,

ease of availability, and potent catalytic activity (Ugale et al., 2022, 16–29).

The main techniques for creating metal oxide nanoparticles are physical and chemical. These methods, however, employ poisonous and highly reactive reducing agents which are bad for plants, animals and the environment. These techniques also provide a number of difficulties because they call for specialized tools, intricate processes, and rigorous experimental settings. Therefore, while chemical methods rely on synthetic agents for capping, reducing, and stabilizing and produce non–eco–friendly byproducts, they produce the desired homogenous metallic nanoparticles. In contrast, physical methods produce heterogeneous nanoparticles with high energy consumption. Furthermore, because of their detrimental impact on human health, nanoparticles made by physical and chemical methods cannot be employed for medical purposes (Ashour et al., 2023, 3356). So, the researchers are looking for the ecofriendly methods to prepare nano metal oxides.

2. The Theoretical Framework

The phrase "green synthesis" describes methods, strategies, and procedures that use the least amount of energy to create nanoparticles while preventing hazardous consequences through cleanup, remediation, control and regulation. The principles of green synthesis include minimizing waste, reducing pollutants and byproducts, using greener (or nontoxic) solvents and auxiliaries, and using renewable feedstock (Singh et al., 2018, 1–24).

Natural extracts are utilized in place of artificial chemicals, and the reaction doesn't require high pressure or temperature. Extracts of natural products include polyphenols and flavonoids from foods and beverages including g–Coffee, tea, and wine, as well as proteins and vitamins.These substances are safe, biodegradable, and have the ability to function as capping and reducing agents, increasing the synthesis of nanoparticles while reducing aggregation (Smuleac et al., 2011, 131–137) (Mohamed et al., 2023, 7227). Fig.2 shows Simple green biosynthesis scheme of nanomaterial formation (Al–Hakkani et al., 2021, e05806).

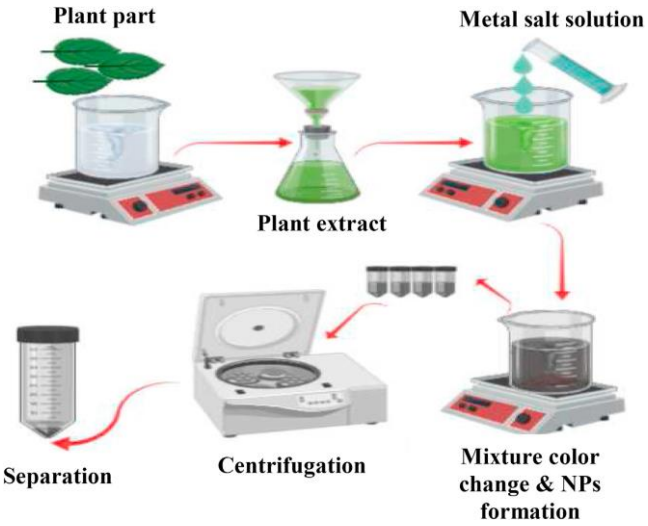

Figure (2): Simple green biosynthesis scheme of nanomaterial formation

The green manufacture of metal oxide nanoparticles has previously employed a number of natural reducing agents. Fang Zhu and his colleagues created

nanomaterials using the green synthesis approach, which used green tea extract as a stabilizing agent and reducing agent. This nanomaterials was then used to treat groundwater contaminated with Cr(VI). With a removal efficiency of 94.7%, nanomaterials effectively extracted Cr (VI) from groundwater at a pH of 5, 303 K and a dosage of 0.4 g/L. Another study used leaf extracts from mulberries, oaks, and cherries to create "green" nanomaterials adsorbents that could remove As (III) and Cr (VI). The produced green nanomaterials was discovered to have nanoparticles between 10 and 30 nm in size (Zhu et al., 2018, 184–190) (Mohamed et al., 2023, 7227).

Because of their distinct physical, electrical, magnetic, and optical properties at nanoscale dimensions (less than a few hundred nanometers) in comparison to their bulk counterparts, transition metal oxides are the focus of attention among scientific communities. The nanoparticles' high surface–to–volume ratio, finite (surface) size effect, and quantum confinement effect are the causes of this. One element that can exist in a variety of forms, from zero to three valence, is iron. Furthermore, the properties of iron compounds vary, ranging from ferromagnetic to magnetic. Magnetite (Fe_3O_4), Goethite (FeO(OH)), Hematite (α–Fe_2O_3), and Maghemite (γ–Fe_2O_3) are iron oxides (IOs) that fall under the category of magnetic nanoparticles (Al–Hakkani et al., 2021, e05806).

Because of their potential uses in a variety of industries, including electronics, biomedicine, and environmental processes, iron oxides are being studied extensively. Over the past fifteen years, magnetic iron oxide nanoparticles have been studied for their many technological uses as well as their intriguing scientific potential in a number of areas, including targeted drug delivery, magnetic hyperthermia, cancer treatment, magnetic resonance imaging (MRI), photocatalysis, biosensing and bioseparation, and agriculture (Kumar et al., 2022, 1–21).

Iron oxide nanoparticles can be made using a variety of well–known techniques. Iron oxide nanoparticles are prepared using around 90% of chemical processes, compared to 8% and 2% for physical and biological approaches, respectively. Additionally, as illustrated in Figure 3, these techniques are separated into smaller groups, making it simple to see the proportion of approaches used to create iron oxide nanoparticles. For the synthesis of iron oxide nanoparticles, each technique offers pros and cons (Ali et al., 2016, 49–67) (Kumar et al., 2022, 1–21).

Researchers have employed plant extracts to create iron nanoparticles, which are then used to adsorb heavy metals from aqueous solutions. Because plant extracts include polyphenols, which are believed to change iron ions into zero–valent iron, they are utilized as reducers. Iron nanoparticles have been created using plant extracts such as clove and green coffee. Eugenol, often referred to as 4–allyl–2–methoxyphenol, is found in cloves and is believed to be the most

prevalent component of clove extract. It serves as an astabilizing and reducing agent for iron nanoparticles (Fe NPs). G–Coffee contains a variety of bioactive substances, such as phenols, alkaloids, flavonoids, polysaccharides, and saponins. These substances, which are present in g–Coffee seed extract, have two functions: they reduce metals and act as capping agents (Lingamdinne et al., 2019, 122–127) (Mohamed et al., 2023, 7227).

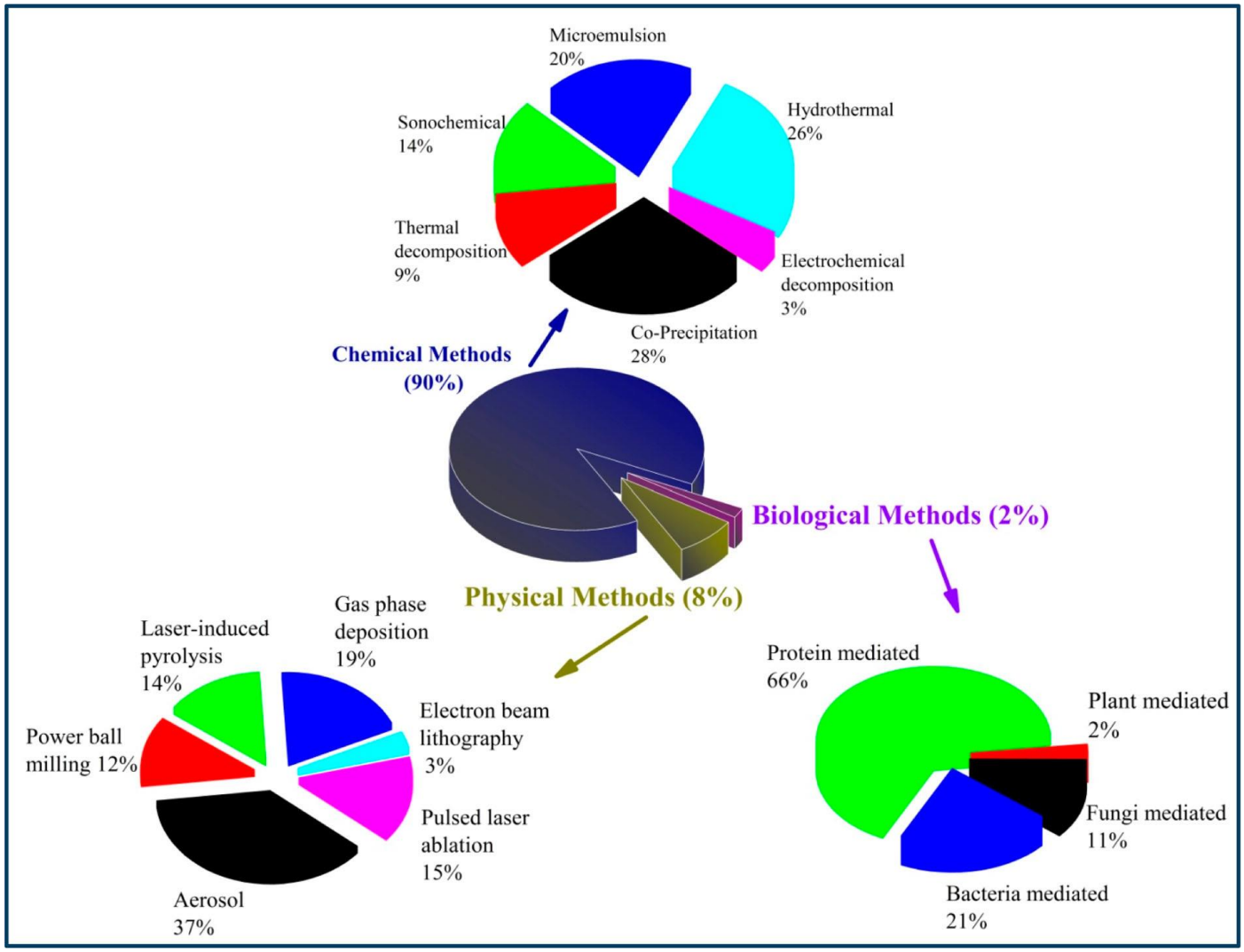

Figure (3): Basic methods of synthesizing iron oxides nanoparticles with the details subcategories modified from

In order to obtain stable and crystalline Fe oxide nanoparticles, the Fe NPs made in this work using the extract from natural products (g–Coffee and clove) were calcined at 550 °C. XRD technology were used to examine the generated iron oxide nanoparticles both before and after calcination. The prepared nanomaterials are applied for environmental application like reduction of dyes such as methylene blue and Remazol red using $NaBH_4$.

3.Methods of Research and the tools used

Materials: Iron (III) nitrate hydrate ($Fe(NO_3)_3.9H_2O$, MW=404 g/mol) was from LOBA Chemie. An extract of green coffee and clove from Egyptian markets has been utilized to reduce iron (III) nitrate salt. Sodium hydroxide was obtained from Piochem for Laboratory Chemicals, Egypt. Sodium borohydride ($NaBH_4$) was from Sigma–Aldrich. Distilled water and ethanol were used as solvents. Dyes like Methylene Blue (MB) and Remazol Red RB–133 (RR) were purchased from Riedel–de Haën AG and DyeStar.

Tools: Beakers, conicals, pipettes, graduated cylinders, funnel, filter paper, centrifuge, thermometer, balance, hot plates with stirring, pH meter, furnace, muffle, X–ray diffraction (XRD) and UV–Visible instrument.

Procedure:

Preparation of Clove and g–Coffee extract: Firstly, to remove dust particles, Clove and g–Coffee were rinsed twice with distilled water before being dried and pulverized into powder. After that, the grinded powder was dissolved in 250 ml of distilled water and heated for 10 minutes at 100°C. After cooling, the supernatant was filtered and the extract solution was stored in a refrigerator at 4°C.

Preparation of iron oxide nanoparticles: After making an aqueous solution of ferric nitrate (10 ml of 0.3 M), add 30 ml of the previously produced extract. 0.10 M NaOH was used to adjust the mixture's pH to 6. The synthesis was conducted at room temperature (around 25 °C) for 10 hours with stirring. After that, the material was centrifuged to collect the nanoparticles. The sample was cleaned three times using distilled water and ethanol to get rid of any unreacted biomolecules. Then, the sample was dried for 24 h at 40°C. The resulting Fe NPs were annealed for 2 h at 550 °C to produce the matching iron oxide nanoparticles. Fig.4 shows the prepation of iron oxide nanomaterials using clove and green coffee extract.

Catalytic reduction of dyes: Methylene blue (MB) and remazol red (RR) dyes were chosen as the target degrading pollutants and $NaBH_4$ was employed as a reducing agent. Following the addition of 0.01g of catalyst to the reaction system, 0.01g of $NaBH_4$ was combined with 3 mL of dye solution (5×10^{-5} M) in the cuvette cell. After that, variations in absorbance at wavelengths of 640 and 520

nm for MB and RR, respectively, were monitored using a UV–vis spectrophotometer. The Lambert–Beer law was then used to calculate the dye concentrations. Also, several comparative tests were studied such as (dye + $NaBH_4$) without a catalyst and (dye + catalyst) without $NaBH_4$.

Additionally, remazole red dye is used to study the reusability of the catalyst. Centrifugation is used to separate the catalyst, which is subsequently cleaned with water for use in the subsequent catalytic run.

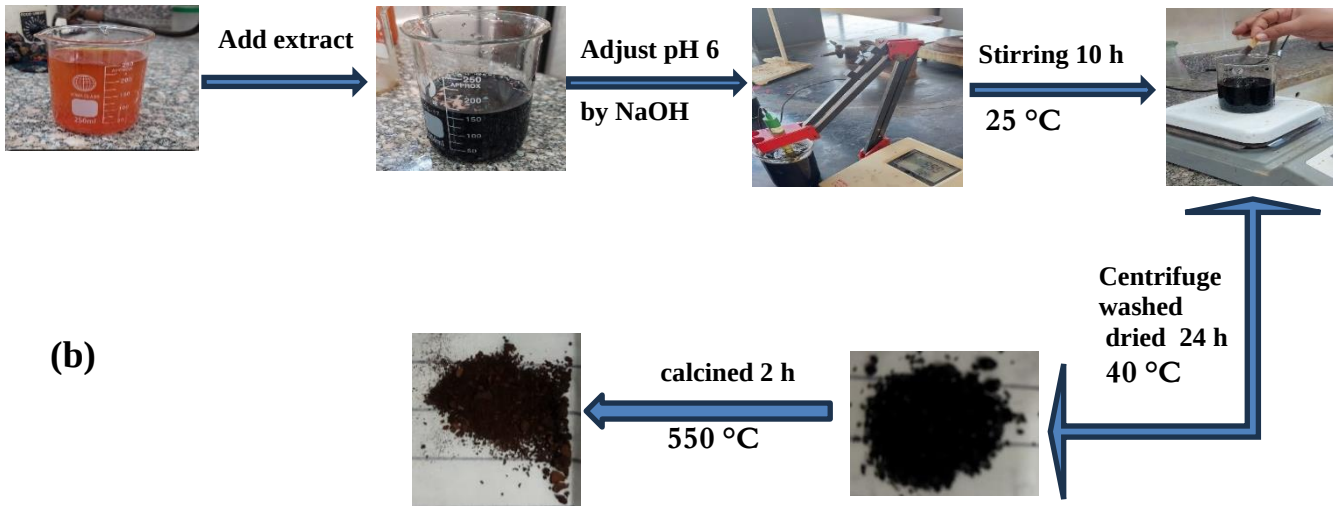

Figure (4): Preparation of Clove and g–Coffee extract(a) and Preparation of iron oxide nanoparticles (b).

4. Results of Research

4.1. Structure analysis

The produced samples' crystal nature, including their size and structure, can be determined using XRD examination. Fig. 5 shows the XRD patterns of nanocatalysts which prepared using clove and green coffee extract. The iron nanoparticles prepared at room temperature without calcination have amorphous structure as shown in Fig.5a. So, it is difficult to determine the exact phase of nanoparticles. Therefore, to form stable and crystalline nanoparticles, the calcination process is essentially. Fig. 5b shows the xrd of iron nanoparticles which prepared using clove and green coffee extract and calcined at 550 °C. It is appeared from this figure that the iron nanoparticles prepared using clove extract has hematite Fe_2O_3 structure (JCPDS No. 33–0664) at 2θ ranges ≈ 24.10°, 33.14°, 35.65°, 40.83°, 49.59°, 54.13°, 57.53°, 62.65°, and 64.32° corresponding to 012, 104, 110, 113, 024, 116, 018, 214, and 300 planes (Fouad et al., 2019, 1253–1261). Also, small diffraction peaks of magnetite are appeared at 30.15, 56.99, 70.97 and 74.95 corresponding to 220, 511, 620 and 622 ((JCPDS No. 19–0629) (Jamshidiyan et al., 35, 1–8). The mean crystal size is calculated using Scherrer equation and it is found 18.1 nm. Also, hematite and magnetite are appeared in sample which green coffee used as extract. The peaks are broader and they have small intensity than sample which clove is used as extract which means small crystal size (12.9 nm).

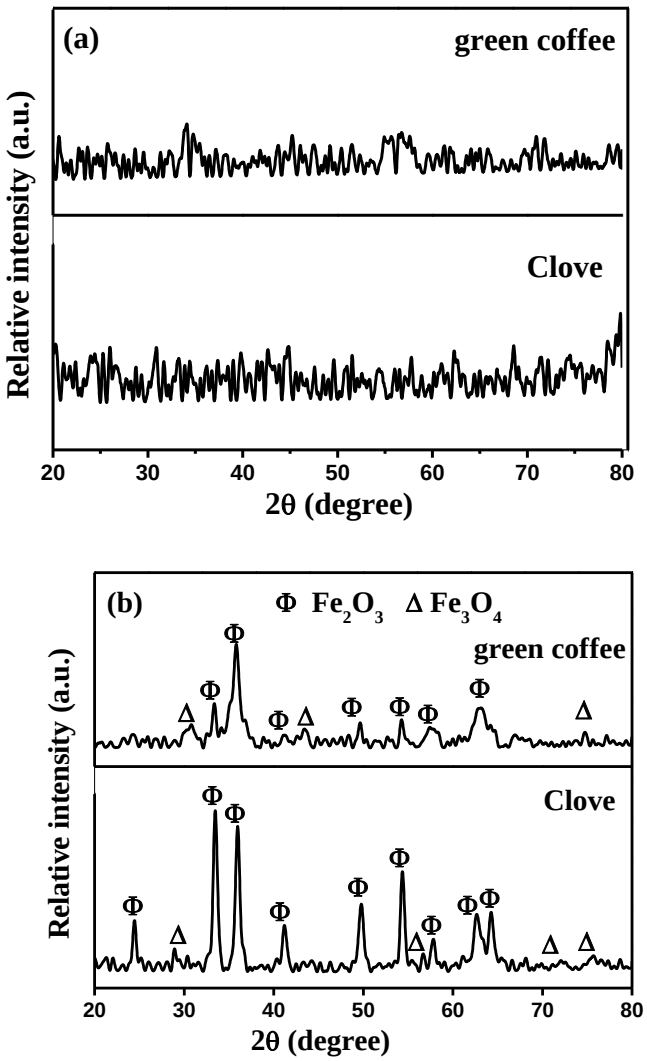

Figure (5): (a) XRD analyses of iron oxide nanoparticles prepared using Clove and green coffee extract at room temperature (a) and calcined at 550 °C (b).

5. Interpretation of Results

5.1. Catalytic reduction of organic dyes

The removal of organic dyes, such as MB and RR, was tested to show the catalytic activity of the prepared catalyst. Fig. 6 and Fig. 7 display the reduction data of MB and RR by nanocatalysts, respectively. The reduction of organic dyes with just iron oxide which prepared using green coffee as extract and calcined at 550 ^{0}C added is shown in Figs. 6a and 7a, and the reduction of organic dyes with only $NaBH_4$ added is shown in Figs. 6b and 7b. It is clear that when iron oxide nanocatalyst was added alone, the organic dye did not diminish even after 50 min. of incubation. Similarly, when the reduction is done in the presence of $NaBH_4$ alone, the dyes' usual absorption peak strength gradually drops over a long period of time. when the organic dye solution is mixed with iron oxide nanocatalyst and $NaBH_4$, the MB and RR solutions totally respond in 2 and 1.30 minutes, respectively as shown in Fig.6c and 7c. As well as turning the MB and RR solutions from blue and red to colorless, respectively.

It was suggested that $BH4^-$ acts as an electron donor, sending electrons to the nanocatalyst, which subsequently sends them to the dye, which is considered an electron acceptor (Benali et al., 2021, 101306). The following formula yields the first–order reaction constants of dye reduction by each catalyst (Figs. 6d and 7d):

$$\ln C_0/C_t = kt$$

C_0: the initial concentration of dye

C_t: the concentration of dye measured at a time t

k: the apparent catalytic rate constant (min^{-1})

Plotting $\ln(C_0/C_t)$ against reaction time (t) yields the apparent catalytic rate constant. Additionally, it was estimated the specific rate constant K' (min^{-1}/g) [the ratio of the rate constant k to the catalyst's weight (W)] [K' = K/W] in Table 1.

The kinetic rate constants of catalytically reducing MB and RR with catalysts are shown in Table 1 and they are followed the order: iron oxide (green coffee 550 °C) > iron oxide (green coffee) > iron oxide (clove 550 °C) > iron oxide (clove). The iron oxide which prepared using green coffee as extract and calcined at 550 ^{0}C has the highest specific rate constant and reaction kinetic rate among them. This is due to small crystal size which mean high surface area (Ibrahim, 2021, 225–236).So, iron oxide is a material with promise for the removal of water pollutants.

5.2 Reusability of the catalyst

The catalyst's capacity to remain stable in reactions for a number of times is one of its practical and economical uses. The iron oxide 's stability which prepared using green coffee as extract and calcined at 550 ^{0}C for remazole red dye reduction was examined. In order to determine the apparent rate constant, four sets of recycling tests were conducted. Recycling data (Fig. 8) indicate a slight drop in apparent rate constant, which is explained by

the catalyst's slight loss following each run and the resulting loss of active sites.

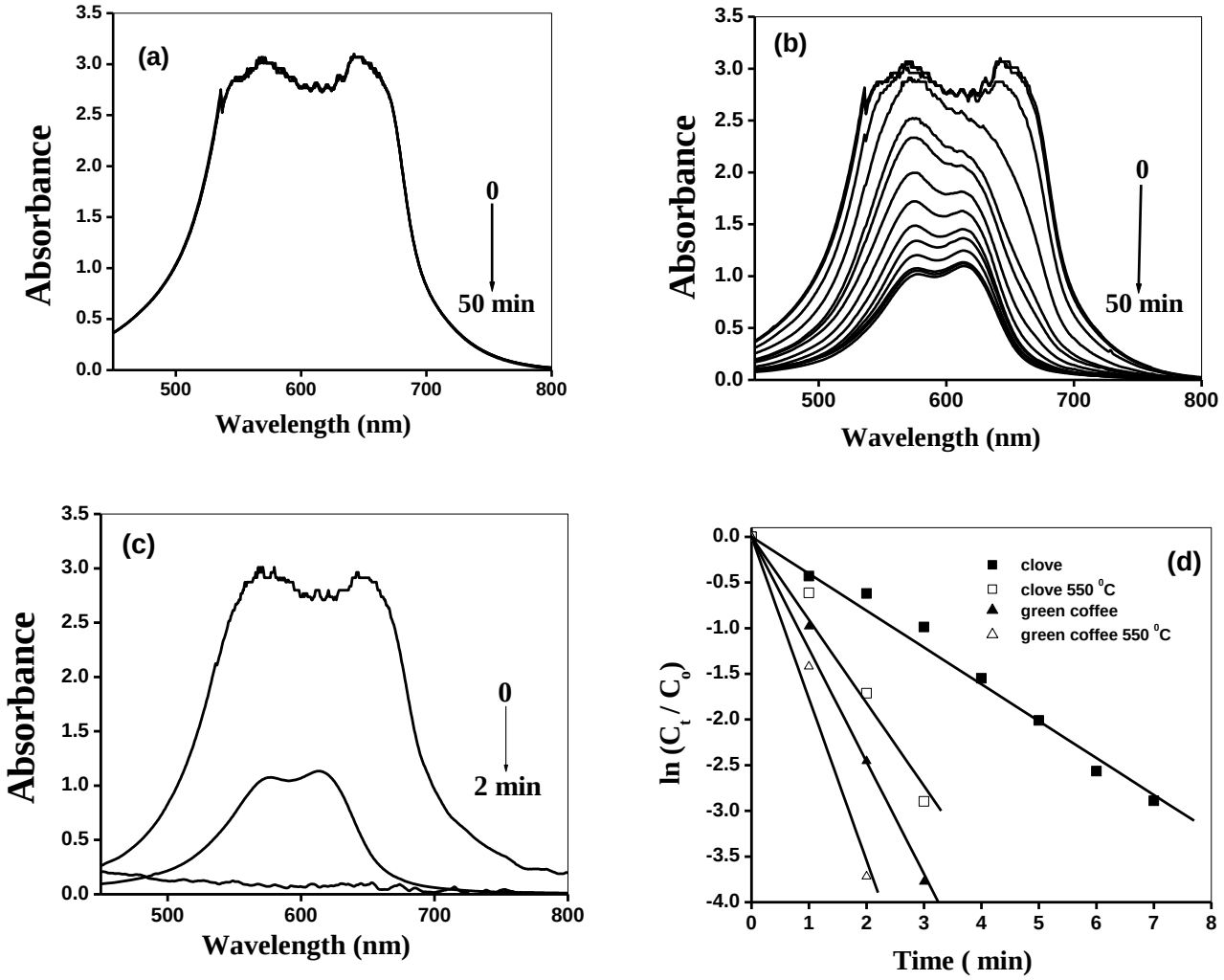

Figure 6: (a) **Reaction absorption spectral of MB with iron oxide (green coffee, 550 °C), (b) Reaction of MB with $NaBH_4$, (c) Reduction of MB with iron oxide (green coffee, 550 °C) and $NaBH_4$ and (d) Plot of ln (C_t/C_0) versus time for Catalytic reduction of MB with all catalysts in the presence of $NaBH_4$.**

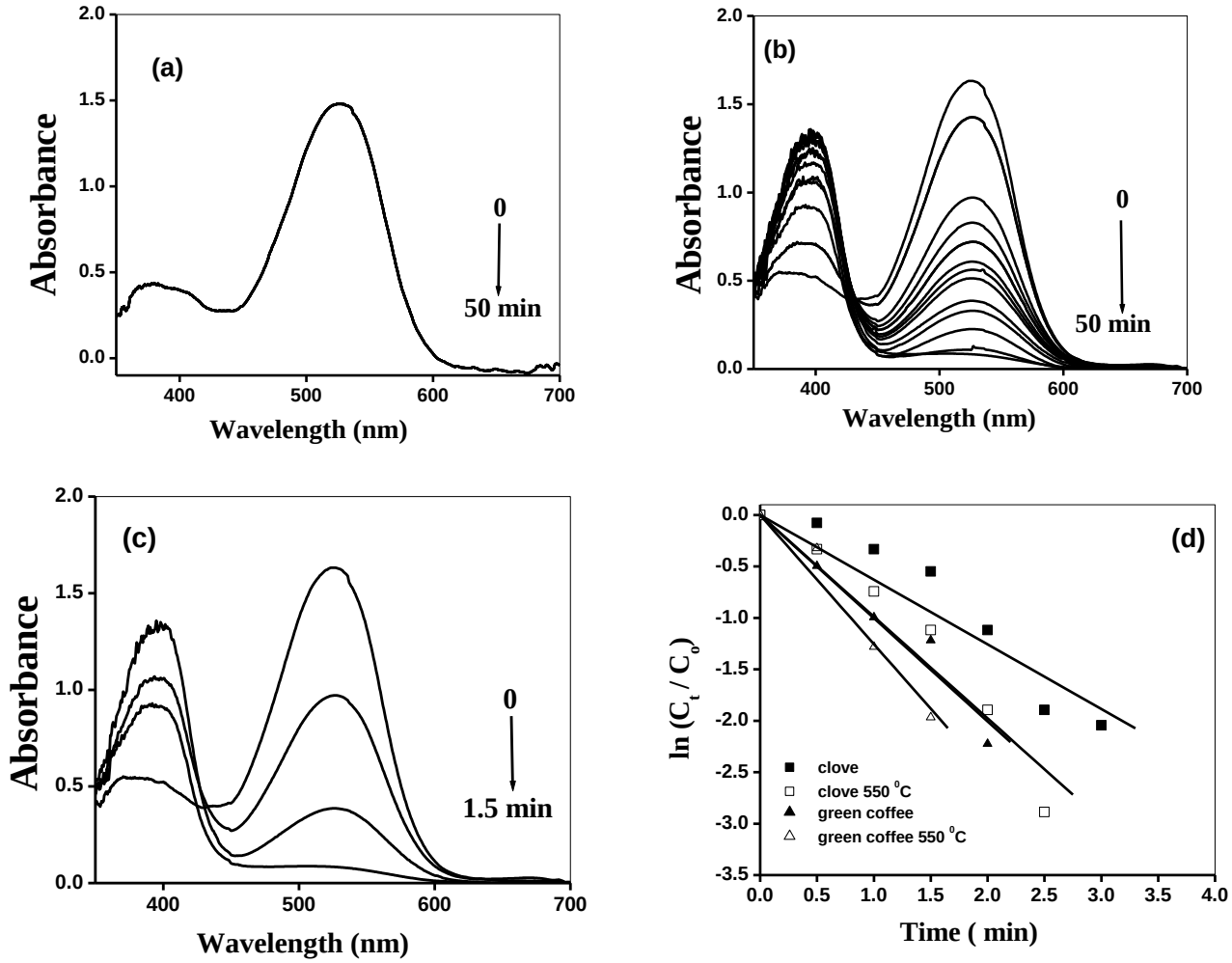

Figure 7: (a) **Reaction absorption spectral of RR with iron oxide (green coffee, 550 °C), (b) Reaction of RR with $NaBH_4$, (c) Reduction of RR with iron oxide (green coffee, 550 °C) and $NaBH_4$ and (d) Plot of ln (C_t/C_0) versus time for Catalytic reduction of RR with all catalysts in the presence of $NaBH_4$.**

Table 1: The kinetic parameters for the reduction of different organic dyes using different prepared catalysts

Methylene blue (MB)				
Sample	**Temperature (°C)**	**Apparent rate constant K (min^{-1})**	**R**	**Specific rate constant K' (min^{-1}/g)**
Green coffee	**Room temperature**	**1.23**	**0.99**	**123**
Green coffee	**550**	**1.77**	**0.99**	**177**
Clove	**Room temperature**	**0.40**	**0.99**	**40**
Clove	**550**	**0.91**	**0.99**	**91**
Remazole red (RR)				
Green coffee	**Room temperature**	**1.02**	**0.98**	**102**
Green coffee	**550**	**1.25**	**0.98**	**125**
Clove	**Room temperature**	**0.62**	**0.97**	**62**
Clove	**550**	**0.98**	**0.97**	**98**

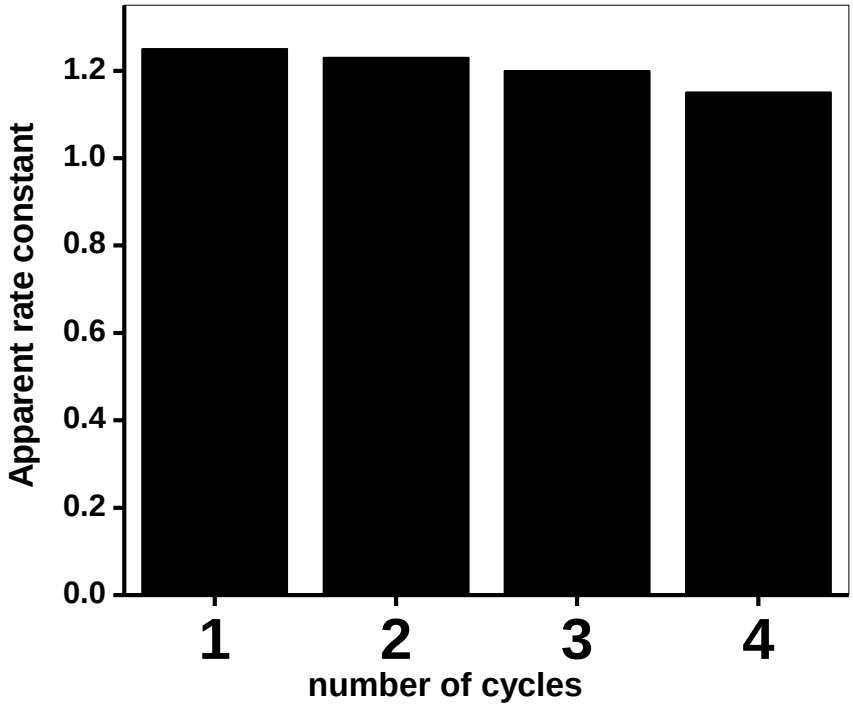

Figure 8: reusability of the catalyst using RR dye.

6. Conclusion

The iron oxide nanocatalysts which prepared using clove and green coffee extract were used to reduction of organic dyes like methylene blue (MB) and remazole red (RR). The catalyst characterization is taken placed by XRD technique. As a result;

– The XRD analysis shows the formation of hematite and magnetite forms of iron oxide after calcination at 550 °C.

–The samples which prepared without calcination have amorphous structures.

– The catalytic activity of the catalysts is tested in reduction of dyes using $NaBH_4$.

– The iron oxide which prepared using green coffee extract and calcined at 550 °C has the highest reduction activity compared with the other studied catalysts.

– The highest catalytic activity is due to small crystal size and high surface area.

– The iron oxide has good stability and durability after multiple runs for reduction of remazole red dye.

Acknowledgement

We would like to express our gratitude to the Physical Chemistry Laboratory and the Department of Chemistry for providing the facilities needed for the project's practical phase. We would

like to express our particular appreciation to our Supervisor Dr/ Marwa Mohamed Ibrahim for her time and efforts she offered throughout the project, her informative comments and recommendations were truly beneficial to us during the project's completion.

References and Sources

Al–Hakkani, M. F., Gouda, G. A., Hassan, S. H.A., 2021. A review of green methods for phyto–fabrication of hematite (α–Fe2O3) nanoparticles and their characterization, properties, and applications, Heliyon, 7,e05806.

Ali, A., Zafar, H., Zia, M., 2016. Synthesis, characterization, applications, and challenges of iron oxide nanoparticles, Nanotechnology Science Applied. 9, 49–67.

Al–tQahani, S. D., Snari, R. M., Alamrani, N. A., Aljuhani, E., Bayazeed, A., Aldawsari, A. M., El–Metwaly, N. M. (2022). Synthesis and adsorption properties of fibrous–like aerogel from acylhydrazone polyviologen: efficient removal of reactive dyes from wastewater, Journal Material Resarch Technology, 18,1822–1833.

Ashour, M., Mansour, A. T., Abdelwahab, M. A., Alprol, A. E. (2023). Metal Oxide Nanoparticles' Green Synthesis by Plants: Prospects in Phyto– and Bioremediation and Photocatalytic Degradation of Organic Pollutants, Processes, 11, 3356.

Benali, F. , Boukoussa B., Ismail, I., Hachemaoui, M., Iqbal, J. , Taha, I., Cherifi, Z., Mokhtar, A., 2021. One pot preparation of CeO_2@Alginate composite beads for the catalytic reduction of MB dye: Effect of cerium percentage, Surfaces and Interfaces,26,101306.

Bruce, N., Perez–Padilla, R., Albalak, R. (2000). Indoor air pollution in developing countries: A major environmental and public health challenge. Bulletin of the World Health Organization, 78, 1078–1092.

Din, M. I., Khalid, R., Hussain, Z., Gul, S., Mujahid, A. (2024). Synthesis and characterization of cobalt doped zinc oxide nanoparticles and their application for catalytic reduction of methylene blue dye, Desalination Water Treatment, 317, 100002.

Ekınc, A. (2020). Hydrogen generation by hydrolysis of $NaBH_4$ with efficient Co–La–Mo–B catalyst for PEM fuel cells, Kinetic Catalysis, 61, 589–594.

Fakioğlu, E., Yürüm,Y., Veziroğlu, T. N. (2004). A review of hydrogen storage systems originated on boron and its compounds, International Journal of Hydrog Energy, 29, 1371–1376.

Fouad, D. E., Zhang, C., El–Didamony, H., Yingnan, L., Mekuria, T. D., Shaha, A. H., 2019. Improved size, morphology and crystallinity of hematite (α–Fe2O3) nano–particles synthesized via the precipitation

route using ferric sulfate precursor, Results in Physics, 12,1253–1261.

Friend, C. M., Xu, B. (2017). Heterogeneous catalysis: a central science for a sustainable future, Accounts of Chemical Research, 50, 517.

Ibrahim, M. M., 2021. An efficient nano–adsorbent via surfactants/dual surfactants assisted ultrasonic co–precipitation method for sono–removal of monoazo and diazo anionic dyes, Chinese journal of chemical engeneering, 40, 225–236.

Ighalo, J. O., Adeniyi, A. G., Adeniran, J. A., Ogunniyi, S. (2021). A systematic literature analysis of the nature and regional distribution of water pollution sources in Nigeria, Journal of Cleaner Production, 283, 124566.

Jamshidiyan, M., Shirani,A.S., Alahyarizadeh, G., 2016 . Solvothermal synthesis and characterization of magnetic Fe_3O_4 nanoparticle by different sodium salt sources, Materials Science–Poland, 35, 1–8.

Kumar, S., Kumar, M., Singh, A., 2022. Synthesis and characterization of iron oxide nanoparticles (Fe_2O_3, Fe_3O_4): a brief review, Contemporary Physics, 1–21.

Lingamdinne, L. P., Koduru, J. R., Karri, R. R., 2019. Green synthesis of iron oxide nanoparticles for lead removal from aqueous solutions, Key Engineering Materials, 805, 122–127.

Mohamed, A., Atta, R. R., Kotp, A. A., Abo El-Ela, F. I. , Abd El-Raheem, H., Farghali, A., Alkhalifah, D. H. M., Hozzein, W. N., Mahmoud, R., 2023. Green synthesis and characterization of iron oxide nanoparticles for the removal of heavy metals (Cd^{2+} and Ni^{2+}) from aqueous solutions with Antimicrobial Investigation, Scientific Reports, 13:7227.

Mohamed, A., Atta, R. R., Kotp, A. A., Abo El-Ela, F. I., Abd El-Raheem, H., Farghali, A., Alkhalifah, D. H. M., Hozzein, W. N., Mahmoud, R. (2023). Green synthesis and characterization of iron oxide nanoparticles for the removal of heavy metals (Cd^{2+} and Ni^{2+}) from aqueous solutions with Antimicrobial Investigation. Scientific Reports,13, 7227.

Naseem, K., Manj, Q.W., Akram, S., Shabbir, S., Noor, A., Farooqi, Z. H., Khan, S. U., Ali, M., Nazar, M. F., Haider, S., Alam, K. (2024). Spectroscopic monitoring of polyurethane–based nanocomposite as a potential catalyst for the reduction of dyes, Spectrochimca Acta A: Molecular Biomolecular Spectroscoppy, 317, 124450.

Patil, K. N., Prasad, D., Manoorkar, V. K., Nabgan,W. B., Nagaraja, M., Jadhav, A. H. (2021). Engineered nano–foam of tri–metallic (FeCuCo) oxide catalyst for enhanced hydrogen generation via $NaBH_4$ hydrolysis, Chemosphere, 281,130988.

Prasad, D., Patil, K. N., Sandhya, N., Chaitra, C. R., Bhanushali, ,J. T., Samal, A. K., Keri, R. S., Jadhav, A. H., Nagaraja, B. M. (2019). Highly efficient hydrogen production by hydrolysis of $NaBH_4$ using eminently competent recyclable Fe_2O_3 decorated oxidized MWCNTs robust catalyst, Applied Surface Science, 489, 538–551.

Priyadharsini, P., SundarRajan, P. K., Pavithra, G., Naveen, S., Kumar, S. S., Gnanaprakash, D., Arun, J., Pugazhendhi, A. (2023). Nanohybrid photocatalysts in dye (Colorants) wastewater treatment: Recent trends in simultaneous dye degradation, hydrogen production, storage and transport feasibility, Journal of Clean. Production, 426, 139180.

Retnamma, R., Novais, A.Q., Rangel, C. M. (2011). Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: a review, International Journal of Hydrogen Energy, 36, 9772–9790.

Rusman, N. A. A., Dahari, M. (2016). A review on the current progress of metal hydrides material for solid–state hydrogen storage application, International Journal of Hydrogen Energy, 41, 12108–12126.

Sadiku, M. N. O., Adebo, P. O., Ajayi–Majebi, A., Musa, S. M. (2020). Environmental Pollution: An Introduction, International Journal of Trend in Research and Development, 7, 155–161.

Salman, M. Pratthana, S., C., Lai, Q., Wang, T., Rambhujun, N., Srivastava, K., Aguey–Zinsou, K.–F. (2022). Catalysis in Solid Hydrogen Storage: Recent Advances, Challenges, and Perspectives, Energy Technology, 10, 2200433.

Singh, J., Dutta, T., Kim, K.–H., Rawat, M., Samddar, P., Kumar, P. (2018). Green'synthesis of metals and their oxide nanoparticles:Applications for environmental remediation, Journal of Nanobiotechnology, 16, 1–24.

Smuleac, V., Varma, R., Sikdar, S. & Bhattacharyya, D. 2011. Green synthesis of Fe and Fe/Pd bimetallic nanoparticles in membranes for reductive degradation of chlorinated organics, Journal of Membrane. Science, 379, 131–137.

Tzanakakis, V. A., Paranychianakis, N. V., Angelakis, A. N. (2020). Water supply and water scarcity. Water, 12, 2347.

Ugale, A. D., Ghodke, N. P., Kang, G., Nam, K., Bhoraskar, S. V., Mathe,V. L., Yoo, ,J. B. (2022). Cost–effective synthesis of carbon loaded Co_3O_4 for controlled hydrogen generation via $NaBH_4$ hydrolysis. International Journal of Hydrogen Energy, 47, 16–29.

Valatin, G., Ovando, P., Abildtrup, J., Accastello, C., Andreucci, M. B., Chikalanov, A., Yousefpour, R.

(2022). **Approaches to cost–effectiveness of payments for tree planting and forest management for water quality services**, **Ecosystem Services**, **53**, **101373**.

Zhu, **F.**, **Ma**, **S.**, **Liu**, **T.**, **Deng**, **X.**, **2018**. **Green synthesis of nano zero–valent iron/Cu by green tea to remove hexavalent chromium from groundwater**, **Journal of Clean Production**, **174**, **184–190**.