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Green Synthesis of Nanoparticles For Sustainable Degradation of Pesticide Contaminants In Water

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Abstract

Pesticides used in agricultural and industrial sectors can be infiltrated into the soil and water causing certain illnesses such as cancer, birth defects, nausea, and weakened immune system. Therefore, studies are directed on methods to deal with contaminated agricultural and industrial wastes. Chemical degradation is one of the most studied methods recently utilized in order to remove these pesticides. The catalyst synthesized using natural resources are proven to be effective and eco-friendly. This study aims to minimize the side effects of the chemical-based nanoparticles and utilize a more sustainable approach such as green synthesis of Ca-Fe_3O_4, Ag- Fe_3O_4, Ca-MgO and Ag-MgO using extracts of Henna, Neem, and Knar leaves, to test these nanoparticle's potential applicability for degrading Dazomet, and to enhance the degradation by synthesizing composite nanoparticles. The degradation was performed using adsorption on 5 mg catalyst in 100 ml of 0.04 M Dazomet solution for a duration of 30 minutes, the results indicated that the Ferrite-based catalysts degraded Dazomet quite effectively than the Magnesium oxide. The Ag- Fe_3O_4 synthesized by Neem and Knar exhibited 67.25% and 54.15% degradation, while via Henna extract displayed leeching thus making it impractical to be compared further. Moving on, the degradation of Ca- Fe_3O_4 prepared with all extracts was relatively insignificant. To optimize Ca- Fe_3O_4, nanocomposite particles of Ag-Ca- Fe_3O_4 in a ratio of 50:50 for Ag :Ca by Neem and Knar were formulated. This illustrated that Knar nanocomposite particles are more efficient with a degradation of 81.09% within 30 minutes.

Keywords—Adsorption, Dazomet, Degradation, Extract, Green Synthesis, Nanoparticles, Sustainable.

I. INTRODUCTION

Rapid industrialization and the widespread use of pesticides in agricultural practices have led to the contamination of water with pesticide residues. Pesticides have been utilized in different industries to enhance agricultural and industrial productivity by eliminating insects, fungus, and herbs. However, the pesticides' contaminated water effect negatively on marine and human lives since it is hard to be removed and it has a long-life span. Pesticides are toxic and can cause serious health issues such as neurological disorders, birth defects and weakened immune system as well as some contaminants can be carcinogenic.

Given that pesticides are toxic and widespread in the environment, it is essential to develop cost-effective and user-friendly treatment processes for their complete degradation. Many methods have been developed for the removal of different harmful pesticides, from wastewater bodies, these may include physical, chemical as well as biological methods. However, some of the conventional methods have certain drawbacks, such as sludge production from membrane filtration and biological treatment which may require special disposal methods, as well as the relatively high cost of some of the methods like coagulation and activated carbon filtration. Therefore, recent research focused on developing nanoparticles that degrade pesticides to less harmful compounds, decreasing the overall cost and achieving higher efficiency.

Nanotechnology applied for environmental remediation follows the global goal of sustainability; the result serves to provide clean water and health for communities that have affected water systems by agricultural runoffs. However, while nanoparticles can be synthesized using chemical-based active ingredients, their negative impact cannot be overlooked. Therefore, it is essential to explore natural, green synthesis alternatives, to reduce the environmental impact and enhance biocompatibility, leading to a more sustainable production process compared to traditional chemical methods.

A. Types of Pesticides

Pesticides are classified according to the type of pests designed to control them. Some types are herbicides, insecticides, and fungicides [1]. Insecticides have a primary purpose in controlling insects such as fleas and mosquitoes. Due to their toxicological effect which could weaken the immune system, and if inhaled or ingested leads to nausea, dizziness, and seizures [2]. Recent researches are directed towards combining them with biological pest-resistant or hybridizing crops to naturally resist pests [1]. One of its critical environmental impacts is affecting the freshwater environments when they enter waterways [3]. Researchers recommend implementing biological control, using resistant

crop varieties alongside chemical treatments to promote sustainable practices [4]. Dazomet is a broad-spectrum soil fumigant, and it is highly soluble in water [5]. In application, it undergoes a chemical reaction that releases a toxic gas called methyl isothiocyanate (MITC). This gas is highly effective in penetrating through the soil and killing pests, pathogens, and weed seeds. Hence, it can be used as Insecticide, Fungicide, and Herbicide [5].

B. Pesticides Removal Methods

37 million people are exposed to pesticides dangers in USA, since 41% of the aquifers used for dinking is contaminated [6]. A study published in Nature's website (2023) [7], revealed that 70,000 tons of pesticides leach into aquifers annually. Therefore, several methods are developed to remove pesticides from contaminated water. Biological removal methods require large area for the set up and associated with high capital cost [8]. On the other hand, physical methods associated with sludge formation and long time for treatment [9]. However, chemical treatment methods, such as adsorption, are used to increase the efficiency of the removal and decrease the total cost [10]. Broadly used catalysts in chemical treatment methods are heterogeneous, due to their ease of separation and high stability, preventing occurrence of side reactions [11]. Furthermore, heterogeneous catalysts can be classified into bulk, micro, and nano particles depending on the size. Both nano and micro particles are used in AOPs, however, nanoparticles have higher surface/volume ratio, hence more surface area available for adsorption [12]. On the other hand, chemical synthesized particles, nano or micro, both release metal in the solution, thus contaminating the solution. That side effect is attributed to the chemical synthesized nanoparticles. Fortunately, methods such as green synthesis are used to limit those drawbacks [13].

II. DESIGN AND IMPLEMENTATION

A. Experimental Work

The experimental work mainly focuses on synthesizing doped iron and magnesium oxide NP's using different plant extracts of Ziziphus Christi (Knar), Lawsonia inermis (Henna), and Azadarichta indica (Neem). Synthesized nanoparticles are employed for the degradation of Dazomet as a representative pesticide.

B. Materials and Equipment

For the synthesis of Ca-Fe_3O_4, Ag- Fe_3O_4, Ca-MgO, Ag-MgO, Ag-Ca- Fe_3O_4 nanoparticles, ferric sulfate Fe2(SO4)3 (76%) and silver sulfate Ag_2SO_4 (99.5%) purchased from Fulka, magnesium sulfate anhydrous $MgSO_4$ (98%) from Scharlau, calcium sulfate $CaSO_4.2H_2O$ (99%) from Fisons. The pesticide studied, Dazomet, was brought in from a facility in Egypt. The extract was prepared using well grinded leaf powder from trees of Lawsonia inermis (Henna), Azadirachta indica (Neem), Ziziphus spina-christi (Knar). The equipment used was digital electronic scale from ae ADAM to weigh, hot plate stirrer (StableTemp) for preparing nanoparticles solution, Laboratory Incubator (B&T Unitemp Benchtop-100ºC) to dry the nanoparticles and leaves for extract preparation, a centrifuge (Labofuge 200, Heraeus) was used to separate the nanoparticles form the solution, a UV spectrophotometer (Shimadzu-1601) to measure the absorbance of pesticide solution before and after degradation, Ultrasonic Bath (Derui) to uniformly disperse the nanoparticles using sonic waves, and Minerallight lamp(UVP) for photocatalysis.

C. Methodology

a) Synthesis of extracts

The active ingredients necessary for the green synthesis of the nanoparticles were extracted from the leaves of three types of plants: Knar, Henna, and Neem. For each plant, 10g of dried and well grinded leaf powder was added to 200 ml of deionized water and continuously stirred for 1 hr. The extraction temperature was maintained between 40- 50 °C. Then, the mixture was then filtered, using Whatman with 185mm diameter, filter paper and carefully stored for further uses [14].

b) Synthesis of nanoparticles

Doped iron oxide nanoparticles are synthesized using the co-precipitation method. A ratio of 2.5:1 doping salt to iron salt is used: for Ag Fe_3O_4 5 g $AgSO_4$: 25 g Fe $(SO_4)_3$, for Ca Fe_3O_4,10.62 g $CaSO_4$: 10 g Fe $(SO_4)_3$. Salts were added to 100 ml deionized water and 50 ml of the leaf extract. the mixtures were continuously stirred while being heated for 1 hour maintaining the temperature at 60-70 °C. After that, the solutions were allowed to settle at room temperature, and then centrifuged for 5 minutes at 5000 rpm with water twice and ethanol once. The samples were then dried for 3 hours at 90 °C, and finally calcinated at 500 °C for 2 hours [15]. Ca-Ag Fe_3O_4 nanocomposites were synthesized in a similar manner except that the calcination temperature was maintained at 700 ºC. Three different Ca-Ag ratios were prepared: 25:75, 50:50, and 75:25 mol Ag to Ca, respectively [16]. While the doped Ca-MgO and Ag-MgO nanoparticles were synthesized using the sol-gel method in ratio of $(X_{0.10}Mg_{0.90}O)$ where X represents Ca and Ag. 30 g of $MgSO_4$ and 3.93 g of $CaSO_4$, or 7.79 g of $AgSO_4$ were added to 500 ml of deionized water and 35 ml of plant extract. the solution was heated at 60-70 °C for 1 hour, while continuously being stirred. Afterwards, the prepared solutions were left to settle for 2 days for the gel to settle down. Subsequently, the settled gels were washed thoroughly with deionized water and ethanol and dried at 90 °C. The formed nanoparticles were then calcinated at 700 °C for 2 hours [17, 18].

D. Equations

The degradation percentage is calculated as per Eq. (1) [19].

$$\%\, Degradation = \frac{C_o - C}{C_o} \times 100 \quad (1)$$

Where C_o is the initial concentration and C is the final concentration.

III. CHARACTERIZATION

The synthesized nanoparticles have been characterized and sized using a Scanning Electron Microscope (SEM). The SEM of Ag- Fe_3O_4 NPs is shown in Fig.1 (A) while Fig. 1 (B) presents that for Ag- MgO NPs both prepared employing Neem leaves extract.

The wide range (10 µm) in the images shows the porous 20 structure of the nanoparticles. The Ag-MgO (Neem) EDS spectrum, Fig.1 (D), proved the existence of Ag, Mg, and O, as the beaks indicates the certainty element exist at the point analyzed. On the other hand, Fig. 1 (C) shows the EDS analysis that characterize Ag-Fe3O4 (Neem) nanoparticles, confirming the presence of that Ag, Fe, and O. Spectra proposes existence of other components such as Cd, S and Si in both samples. These impurities can be from insufficient sample preparation and quality of deionized water used, since Cl and Si can be found in the tap water.

A closer picture of Ag-MgO is shown in Fig. 2, where the size of the particles is ranged between 15-55nm which is within the range of green NPs mentioned in the literature and goes hand to hand with the results obtained by A.B.Habtemariam (2022) where WO3 synthesized by Rhamnus Prinoides Leaf Extract is characterized, and the size was found around 60 nm [20].

Moreover, comparing the nanoparticle morphology synthesized using different plant-based extracts, Fig. 3 (A) and (B) are images of Ag-Ca- Fe_3O_4 (50:50) produced using Knar and Neem, respectively. While the particles fall within the nanoparticle size range, they demonstrate an uneven particle size distribution. Figure 4 (A) and (B) presents ferrite composite nanoparticles with Ag:Ca ratio of 25:75 and 75:25, respectively. Analyzing the morphology of the two NPs, Fig. 4 (A) and (B) shows irregular and nonuniformed shaped particles, which indicates Fe_3O_4 NPs aggregation caused by dipole-dipole interaction of the particles, this agrees with the findings of M.Faruruwa et al. (2024).

Furthermore, the edges in B appear smoother, with less distance between the grains. Moreover, Fig. 4 (C), (D) and (E) are rich in silver while same contaminants coexist in all spectrums, which indicates that both NPs are synthesized from the same extract. However, Ag exists in low concentrations compared to Ca in Fig. 4 (C), unlike Fig. 4 (D), which elaborates on the preferred ratios mentioned.

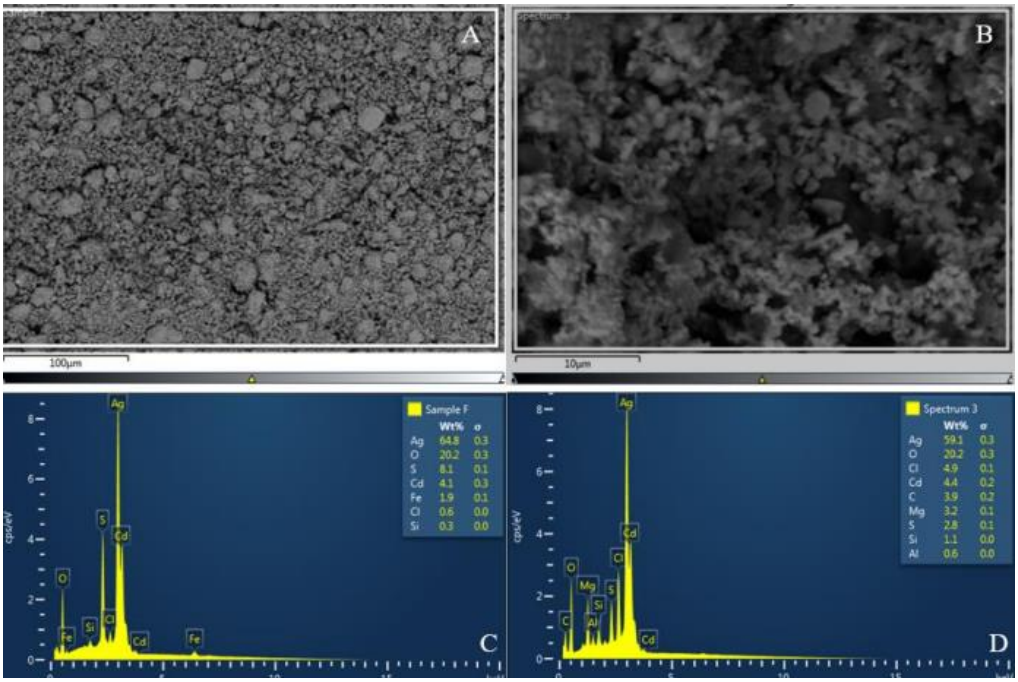

Figure 1 SEM of Ag-MgO and Ag- Fe_3O_4 with Neem A) Ag- Fe_3O_4 NPs (Neem), B) Ag- MgO NPs (Neem), C) EDS analysis of Ag- Fe_3O_4 NPs (Neem), and (D) EDS analysis of Ag- MgO NPs (Neem).

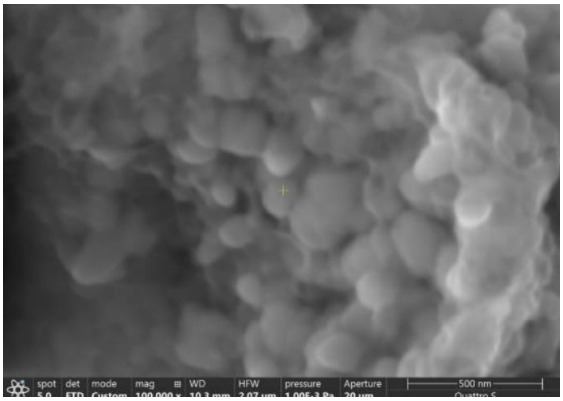

Figure 2 SEM image of Ag-MgO particles

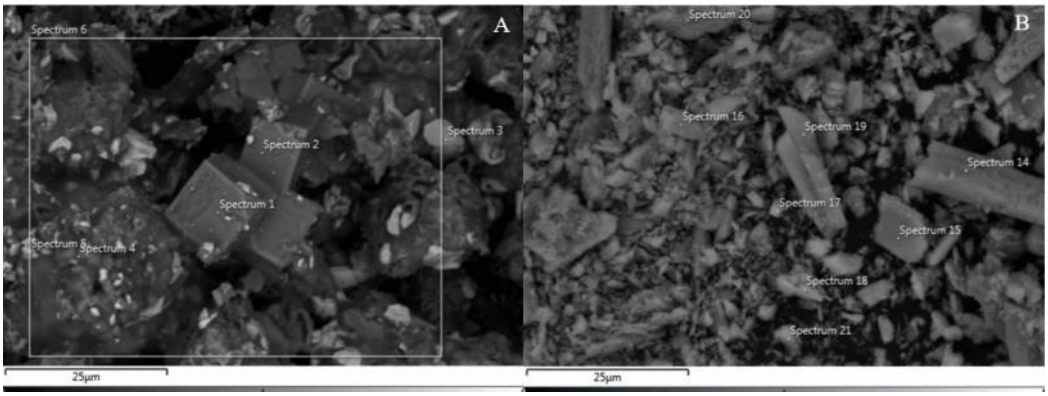

Figure 5 SEM of composite (50:50) nanoparticles with different extracts A) Composite Ag-Ca- Fe3O4 NPs (Knar) 50:50, B) Composite Ag Ca- Fe3O4 NPs (Neem) 50:50.

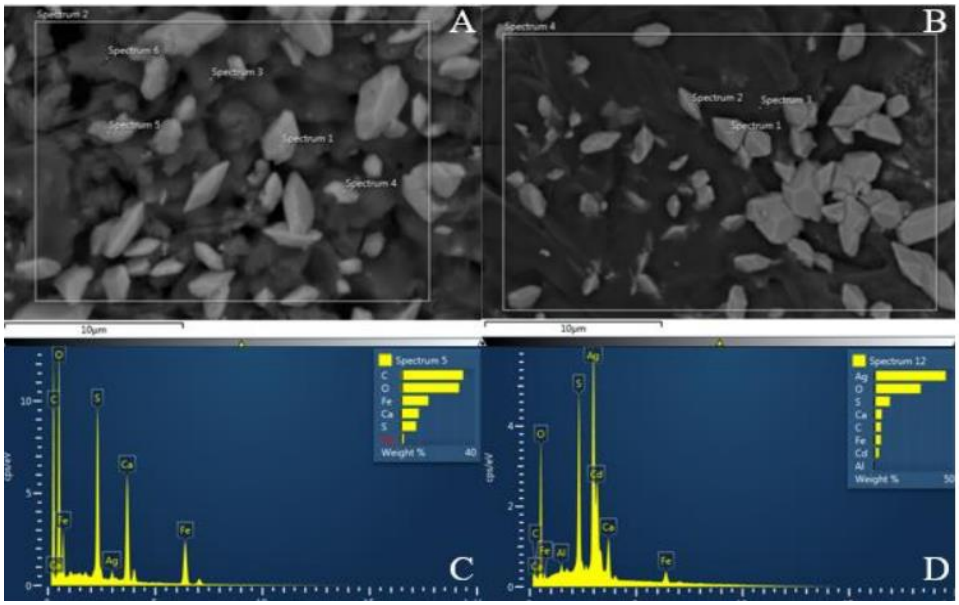

Figure 4 SEM of composite nanoparticles A) Composite Ag-Ca- Fe_3O_4 NPs (Knar) 25:75, B) Composite Ag-Ca- Fe_3O_4 NPs (Knar) 75:25.

Table 1 Dazomet adsorption results

Nanoparticle	Plant extract	Time (min)	Percentage degradation (%)	Time (min)	Percentage degradation (%)
Ag-Fe_3O_4	Henna	10	30.70	30	62.07
	Neem	10	65.01	30	67.25
	Knar	10	42.58	30	54.15
Ca-Fe_3O_4	Henna	10	No degradation	30	No degradation
	Neem	10	No degradation	30	No degradation
	Knar	10	1.42	30	1.79
Ag-MgO	Henna	10	44.06	30	50.05
	Neem	10	20.08	30	21.36
	Knar	10	50.40	30	51.89
Ca-MgO	Henna	10	No degradation	30	5.51
	Neem	10	0.81	30	2.28
	Knar	10	1.58	30	1.15

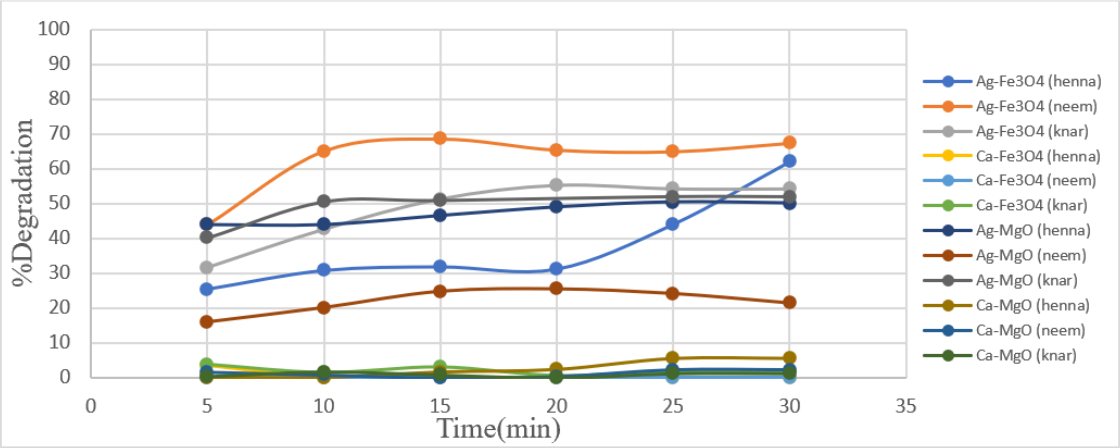

Figure 6 Percentage degradation vs. Time for Dazomet by adsorptionTime for adsorbing Dazomet

IV. Results and Discussion

The synthesized nanoparticles from different plant-based extracts were investigated for their pesticide adsorption efficiencies for the removal of Dazomet.

In all following sections, the percentage degradation was calculated using Eq. 1.

A. Adsorption

To measure the adsorption efficiencies of the synthesized nanoparticles when they were used as nano-adsorbents, Table 1 was conducted at two adsorption time durations.

Based on Table 1 results, it clearly verifies the effectiveness of Ag doped nanoparticles for pesticide adsorption. The adsorption efficiencies ranged from 20.08% to 65.01% at 10 minutes and increased to a range of 21.36% to 67.25% in 30 minutes, further approving the availability of the active surface area for adsorption. However, Ca doped nanoparticles had shown none or insignificant pesticides adsorption capabilities, perhaps their catalytic properties were not sufficient to initiate the adsorption. Therefore, based on adsorption method it can be concluded that combining Ag with both Fe_3O_4 and MgO has enhanced the overall adsorption properties of the nanoparticles, while the presence of Ca in both bases did not provide a significant contribution to the adsorption efficiency. Moreover, Table 1 shows that Ag-Fe_3O_4 synthesized by Neem extract gave the highest adsorption efficiency (67.25%) among the three plant extracts used, and obviously a fastest rate. For Ag-MgO nanoparticles, the use of both Henna and Knar extracts resulted in very close adsorption efficiencies, in contrast NPs produced by Neem based extract showed lower adsorption capability. Figure 5 visualizes the rate and percentage pesticide removal of all nanoparticles within a duration of 30 minutes.

In Fig. 5, it looks like the degradation decreases in some points, regardless of that, it continues to increase. In addition, Ag-MgO (Neem) and Ag-Fe_3O_4 (Neem), for example, reaches saturation and then starts to fluctuate, which compliances with the behavior of monolayers [21]. Ag doped Nanoparticles synthesized by all plant-based extracts, when added to the pesticide solution, changed the color of the solution. This indicates the probability of a by-product formation. However, this color faded out with time indicating its degradation in the presence of the nanoparticles. Moreover, the experimental work contains a few random errors which may affect the results, such as the presence of impurities in the cell surface, that is used to read the absorbance, effect on the readings accuracy.

B. *Composite Nanoparticles*

The previous study showed that Ag-Fe_3O_4 produced via all three plant extracts displayed significant removal efficiencies, while Ca-Fe_3O_4 nanoparticles displayed no degradation at all. Therefore, to enhance the adsorption properties Ca-Fe_3O_4 nanoparticles, composite Ag-Ca-Fe_3O_4 nanoparticles were prepared with a ratio of 50:50 of silver to calcium as per literature. The composite Ag-Ca-Fe_3O_4 nanoparticles (50:50) were prepared using both Neem and Knar extracts, since Henna extract did not provide comparative results as the curves were all shifted from origin. From the adsorption experiment it was clearly illustrated that the composite Ag-Ca-Fe_3O_4 nanoparticles (50:50) prepared with knar extract have a higher saturation percentage of Dazomet as shown in Fig. 6. Therefore, Knar was selected for further experiments.

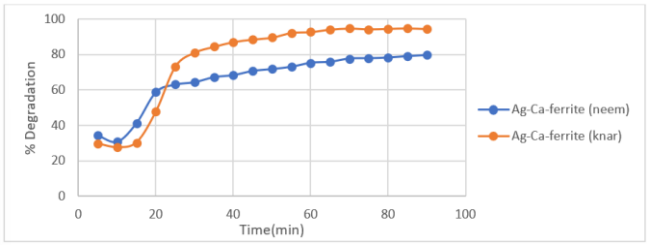

Figure 7 Adsorption using 5 mg composite Ag-Ca- Fe_3O_4 nanoparticles (50:50) in 0.04g/L dazomet solution

Considering that presence of silver enhanced the Ca-Fe_3O_4 nanoparticles adsorption properties, it was further tested that how the amount of silver affects the efficacy of the composite Ag-Ca-Fe_3O_4 nanoparticles. According to literature, composite Ag-Ca-Fe_3O_4 nanoparticles with Knar extract were prepared with ratios of 25:75 and 75:25, for silver to calcium, correspondingly. As it can be seen from Fig. 7, the results of the adsorption process demonstrated that the composite nanoparticles with the ratio of 75:25 has a higher rate of degradation than the other ratios hence proving that amount of silver nanoparticles play a significant role in enhancing quality of the composite Ag-Ca-Fe_3O_4 nanoparticles.

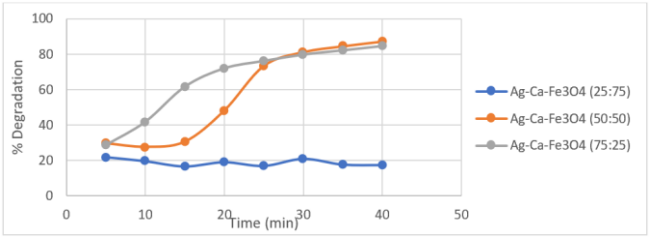

Figure 8 Adsorption using 5mg composite Ag-Ca- Fe_3O_4 nanoparticles (Knar) in 0.04g/L dazomet solution

It is also visible from Fig. 8 that combining calcium and silver ferrite nanoparticles not only resulted in higher degradation than Ca-Fe_3O_4 nanoparticles but also outperformed that of Ag-Fe_3O_4 nanoparticles (Fig. 8 (A)). Additionally, the composite Ag-Ca-Fe_3O_4 (75:25) nanoparticles with Knar extract also displayed better degradation percentages in adsorption as compared to Ag-MgO Henna, Neem, and Knar (Fig. 8 (B)).

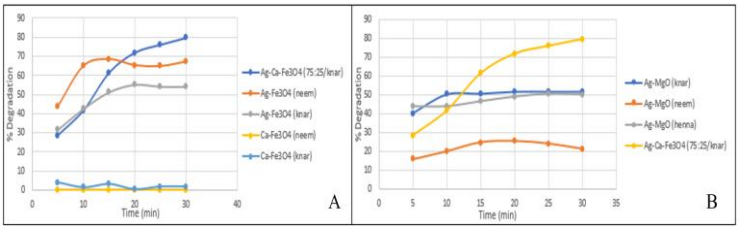

Figure 9 Adsorption results of composite Ag-Ca-Fe_3O_4 nanoparticles comparative to single doped nanoparticles A: Compared to ferrite-based NPs and B: Compared to magnesium oxide-based NPs

V. CONCLUSION

The study was successful in synthesizing and testing green synthesized NPs using different plant extracts: Neem, Knar, and Henna. The synthesized NPs were tested for the degradation of pesticide contaminants in water, with a focus on the development of composite nanoparticles to enhance the degradation process. Characterization of the synthesized particles confirmed the assumed compositions for both single and double-doped NPs, although the particle sizes varied due to factors inherent in green synthesis methods.

The single-doped NPs showed variable success in degrading Dazomet, with Ag-Fe_3O_4 combined with Neem extract having the highest degradation rate of 67.25%. In contrast, Ca-Fe_3O_4 and Ca-MgO with all extracts showed less than 10% adsorption after 30 minutes.

To enhance the catalytic properties of the Ca dopant, composite NPs were synthesized. As compared to Neem, the composite Ag-Ca-Fe_3O_4 NPs (50:50) synthesized via Knar extract exhibited a higher saturation concentration of 94.48%. The composite Ag-Ca-Fe_3O_4 NPs (75:25) synthesized with Knar achieved a degradation of 84.42% in 40 minutes, by using 5 mg NPs in 100 ml of pesticide solution at a concentration of 0.04 g/L.

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REFERENCES

[1] "fungicide | Britannica," Encyclopedia Britannica, 2019. https://www.britannica.com/science/fungicide/additional-info [Accessed: Apr 01, 2024].

[2] "Dazomet - an overview | ScienceDirect Topics," www.sciencedirect.com. https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/dazomet

[3] T. Brown, "Agricultural fungicides: Impact on long-term food and biological security," House of Lords Library, Nov. 20, 2023. https://lordslibrary.parliament.uk/agricultural-fungicides-impact-on-long-term-food-and-biological-security/ [Accessed: Apr 03, 2024].

[4] T. S. Thind, "Changing trends in discovery of new fungicides: a perspective," Indian Phytopathology, vol. 74, no. 4, pp. 875–883, Aug. 2021, Available: https://doi.org/10.1007/s42360-021-00411-

[5] University of Hertfordshire, "Dazomet (Ref: N 521)," Herts.ac.uk, 2024. https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/203.htm?form=MG0AV3 [Accessed: Apr 04, 2024].

[6] "Millions of People Drinking Groundwater with Pesticides or Pesticide Degradates - Beyond Pesticides Daily News Blog," *Beyond Pesticides Daily News Blog*, Jan. 15, 2021. Millions of People Drinking Groundwater with Pesticides or Pesticide Degradates - Beyond Pesticides Daily News Blog [Accessed Apr 4, 2024].

[7] L. Low, "Global analysis shows how pesticides leach into the environment," *The University of Sydney*, Jul. 13, 2023. Available: Global analysis shows how pesticides leach into the environment - The University of Sydney

[8] S. N, "Activated Sludge Treatment - Definition, Notes & Process," Biology Reader, Oct. 23, 2020. https://biologyreader.com/activated-sludge-treatment.html

[9] A. Marican and E. F. Durán-Lara, "A review on pesticide removal through different processes," *Environmental Science and Pollution Research*, vol. 25, no. 3, pp. 2051–2064, Nov. 2017, Available: https://doi.org/10.1007/s11356-017-0796-2.

[10] I. A. Saleh, N. Zouari, and M. A. Al-Ghouti, "Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches," *Environmental Technology & Innovation*, vol. 19, p. 101026, Aug. 2020, Available: https://doi.org/10.1016/j.eti.2020.101026.

[11] S. Cao, F. (Feng) Tao, Y. Tang, Y. Li, and J. Yu, "Size- and shape-dependent catalytic performances of oxidation and reduction reactions on nanocatalysts," *Chemical Society Reviews*, vol. 45, no. 17, pp. 4747–4765, 2016, Available: https://doi.org/10.1039/c6cs00094k.

[12] D. P. Otto and M. M. de Villiers, "Why is the nanoscale special (or not)? Fundamental properties and how it relates to the design of nano-enabled drug delivery systems," *Nanotechnology Reviews*, vol. 2, no. 2, pp. 171–199, Apr. 2013, Available: https://doi.org/10.1515/ntrev-2012-0051.

[13] "Nanoparticle & microparticle synthesis," Nanoparticle & Microparticle Synthesis [Accessed: Apr 12, 2024].

[14] "Synthesis of WO3 Nanoparticles using Rhamnus Prinoides Leaf Extract and Evaluation of its Antibacterial Activities," Biointerface Research in Applied Chemistry, vol. 12, no. 1, pp. 529–536, Apr. 2021, Available: https://doi.org/10.33263/briac121.529536.

[15] M. A. Albalah, Y. A. Alsabah, and D. E. Mustafa, "Characteristics of co-precipitation synthesized cobalt nanoferrites and their potential in industrial wastewater treatment," SN Applied Sciences, vol. 2, no. 5, Apr. 2020, Available: https://doi.org/10.1007/s42452-020-2586-6.

[16] Sadaf Bashir Khan, S. Irfan, and S. Lee, "Influence of Zn+2 Doping on Ni-Based Nanoferrites; (Ni1−x ZnxFe2O4)," Nanomaterials, vol. 9, no. 7, pp. 1024–1024, Jul. 2019, Available: https://doi.org/10.3390/nano9071024.

[17] Noha Al-Awaji, Moufida Boukriba, Abuzar Albadri, M. Ali, M. Bououdina, and Abueliz Modwi, "Green Ca-Loaded MgO Nanoparticles as an Efficient Adsorbent for Organic Hazardous Dyes," Journal of Nanomaterials, vol. 2022, no. 1, Jan. 2022, Available: https://doi.org/10.1155/2022/5062752.

[18] Q. Fan, H. Yu, T.-G. Wang, Z. Wu, and Y. Liu, "Preparation and Isothermal Oxidation Behavior of Zr-Doped, Pt-Modified Aluminide Coating Prepared by a Hybrid Process," Coatings, vol. 8, no. 1, p. 1, Dec. 2017, Available: https://doi.org/10.3390/coatings8010001.

[19] Z. Mohammad Redha, H. Abdulla Yusuf, S. Burhan, and I. Ahmed, "Facile synthesis of ZnO nanospheres by co-precipitation method for photocatalytic degradation of azo dyes: optimization via response surface methodology," International Journal of Energy and Environmental Engineering, vol. 12, no. 3, pp. 453–466, Mar. 2021. Available: https://doi.org/10.1007/s40095-020-00380-y

[20] "Synthesis of WO3 Nanoparticles using Rhamnus Prinoides Leaf Extract and Evaluation of its Antibacterial Activities," Biointerface Research in Applied Chemistry, vol. 12, no. 1, pp. 529–536, Apr. 2021, Available: https://doi.org/10.33263/briac121.529536.

[21] Y. S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, no. 5, pp. 451–465, Jul. 1999, Available: https://doi.org/10.1016/s0032-9592(98)00112-5.