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Green Synthesis Of (Zn-Fe, Zn-Cu, Zn-Fe-Cu) Nanoparticles Using Pomegranate Peel Extract And Its Application In Wastewater Treatment

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Abstract : The biosynthesis of Zinc-Iron oxide nanoparticles, (Zn-Fe, Zn-Cu, Zn-Fe-Cu) was done under alkaline conditions (pH 12) and temperature ≥ 80 ◦C using Pomegranate aqueous peel extract. This Nanoparticles used in reaction as Catalyst. Also used as dye degrading agents using solar power. The PPE (Pomegranate peel extract) acts as a reducing agent used in synthesis of Zn-Fe, Zn-Cu, Zn-Fe-Cu in Nano-scale size via easy and simple method. This process of synthesis of nanoparticles is useful as they do not lead to any by-product's, also this method is cost effective and do not need any additional chemical for stabilization of particles.

IndexTerms **-** Nanoparticles, Zn-Fe-Cu, Punica granatum L, Green synthesis, wastewater treatment, Nano-catalyst.

INTRODUCTION

Every day, thousands of tons of fruits are consumed worldwide. These wastes can be utilized as sorbents of heavy metals (HM) from wastewater. The World Health Organization (WHO) estimates that 80% of health issues in humans are caused by poor quality drinking water [1]. Water treatment and purification for different impurities is an emerging problem nowadays that calls for the use of innovative techniques together with resource saving and environmentally benign technologies. These strategies need to provide the solution to treat the water for recycling in manufacturing procedures, thereby reducing the amount of freshwater use [1-2]. Waste water treatment solutions have been developed as a result of the pollution produced by the dye and textile industries. These techniques might not work for all pollutants, though. It has been revealed recently that sophisticated oxidative processes can break down dyes into non- toxic by-products. An effective and affordable technique for organic compound breakdown reactions is photocatalysis. Numerous kinds of photocatalysts, such as zinc oxide, which possesses intriguing optical characteristics, have been studied. Nanotechnology has received a great deal of attention recently from a variety of sectors, including biotechnology, chemistry, physics, engineering, medicine, and the material sciences. Conventional techniques for preparing zinc oxide nanoparticles have a number of drawbacks. Chemical and physical methods for synthesizing nanoparticles have few drawbacks, including costly chemicals, hazardous reaction conditions, extended reaction times, and laborious isolation procedures. Subsequently, there is a need to develop novel methods for synthesizing nanoparticles that utilize affordable reagents, environmentally friendly, and less severe reaction conditions [3-7]. Using microbes, fruits, bacteria, fungi, algae, and plants, the green synthesis technology enables the formation of ZnO NPs devoid of contaminants. These methods are safe, economical, biocompatible, environmentally friendly, and green [8]. Iron-based nanoparticles (FeNPs) are widely utilized for their unique characteristics like enhanced reactivity and surface area. By using biocompatible and eco-friendly compounds, it is possible to synthesis them without using hazardous agents or producing harmful by-products. The conventional synthesis process uses sodium borohydride to reduce ferrous or ferric salts, which has undesirable effects on the environment and human health. A different strategy based on the ideas of green chemistry has been applied, utilizing naturally occurring bio-renewable waste materials. FeNPs have a broad variety of various applications, such as water treatment, environmental remediation, biomedicine, electronics, magnetic bio-separation, and catalysis. Although the detrimental consequences of nanoparticles are still mostly unknown, nothing is known about their ecotoxicological characteristics, and even the ecotoxicity of green produced iron oxides (NPs) [9]. Metal nanoparticles have potential applications in various fields such as recording media, microelectronics, and information storage devices. Copper is the most extensively used metal nanoparticle due to its various applications [10-14].

Blends of Zn-Fe, Zn-Cu NPs are synthesized by this technology earlier. In thirst of finding better catalyst for photocatalytic dye degradation, herein we successfully synthesized the blend of Zn-Fe-Cu. These were compared for use in photo-catalyzed dye degradation reactions.

MATERIALS AND METHODS

Materials:

Potassium hydroxide, Methylene orange, Sulphides of the Zinc, Iron, and Copper are acquired from PCL. Hydrogen peroxide was procured from maa saptshrungi chemicals. Pomegranate peels was collected from local juice centers.

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Methods:

Preparation of pomegranate peel extract (PPE)

Pomegranate peels washed two to three times with fresh water. And dried under sunlight, grinded by blender until it got powder and kept at 4˚C until use.

Ten grams of pomegranate peel powder (dried) was stirred at 60 -70◦C for 30 minutes with 100 mL of deionized distilled water in 250 ml conical flask, and then left at room temperature overnight. The solid remnants were separated by filtration and filtrate was centrifuged at 4000 rpm for 15 minutes. This process was repeated three times, then the solution was collected in a sterile container. Aqueous extract was kept at 4˚C until further use.

Green synthesis of Zn-Fe, Zn-Cu, Zn-Fe-Cu Nanoparticles:

Firstly, 0.1 M of solutions of $ZnSO_4$, $FeSO_4$, and CuSO4 were prepared using distilled water.

The solutions of $ZnSO_4$ and $FeSO_4$ (100 mL) were taken in the ratio of 2:1 in 250 mL conical flask. This was stirred at 60 °C for 4 hours on magnetic stirrer. Then the PPE was added dropwise under stirring.

The color change was observed from yellow to black as the extract came in contact with the solution. More PPE was added maintaining basic pH by adding KOH. It was then stirred continuously for 2 more hours. Thus formed reaction mass was kept overnight at room temperature. The precipitate was separated by centrifugation at 4000 rpm for 20 minutes. The pellets were collected and washed twice with distilled water. Thus formed pellets of Zn-Fe nanoparticles were dried at 60 ˚C.

The similar procedure was followed to obtain the Zn-Fe-Cu and Zn-Cu nanoparticles. In case of Zn-Cu nanoparticle preparation, 1:1 ratio of solutions was taken (the blue color of solution changed to black). The solutions' ratio for Zn-Fe-Cu was 1:1:1 and the color change was from blue to green.

RESULTS AND DISCUSSION

For our delight the nanoparticles were successfully synthesized with all variables of metal solutions. This was witnessed by UV visible and IR spectroscopic methods.

UV-visible spectroscopy

The UV-visible spectra supports formation of NPs using PPE. UV-visible spectra is usually obtained to confirm the formation of NPs. Because the presence of Surface Plasmon Resonance (SPR) effect, conducting electrons start vibrating at a certain wavelength range. The spectra were obtained between 200 to 700 nm.

Conducting electrons beginning oscillating at a specific wavelength range resulted from surface plasmon resonance (SPR) effect. The peak obtained at 360.12 nm illustrates the presence of ZnNPs, the peak obtained at 340 nm illustrates the presence of FeNPs, and the peak obtained at 470 nm illustrates the presence of CuNPs in the mixture.

The formation of Zn-Fe nanoparticles were evident from the peaks obtained at 360.12 nm (Zn) and 340 nm (Fe) in spectra obtained for the same (figure 1).

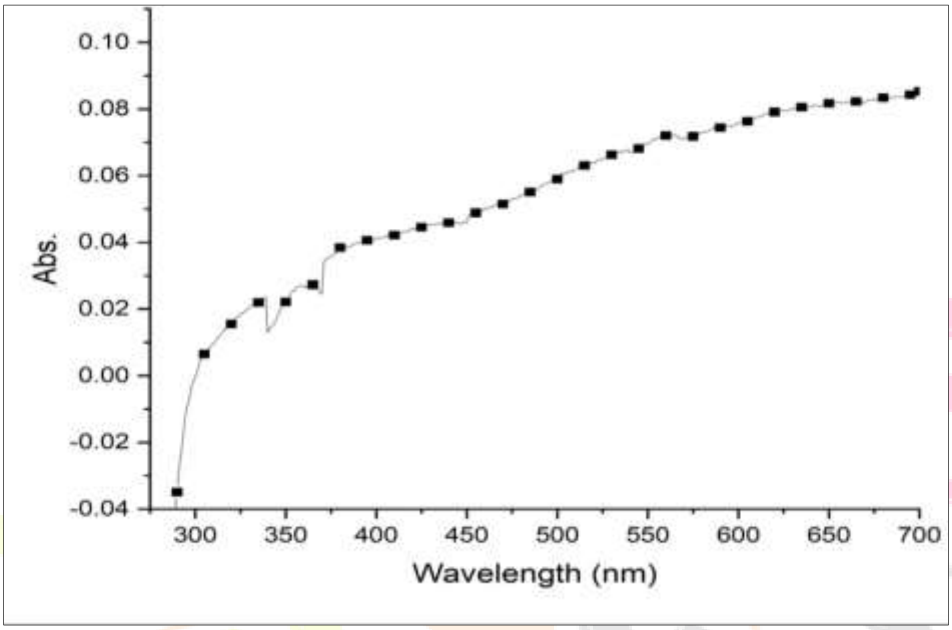


Figure 1: UV-Visible spectra of Zn-Fe nanoparticles

The figure 2 illustrates the formation of Zn-Cu NPs as the absorption peaks are obtained at 360 and

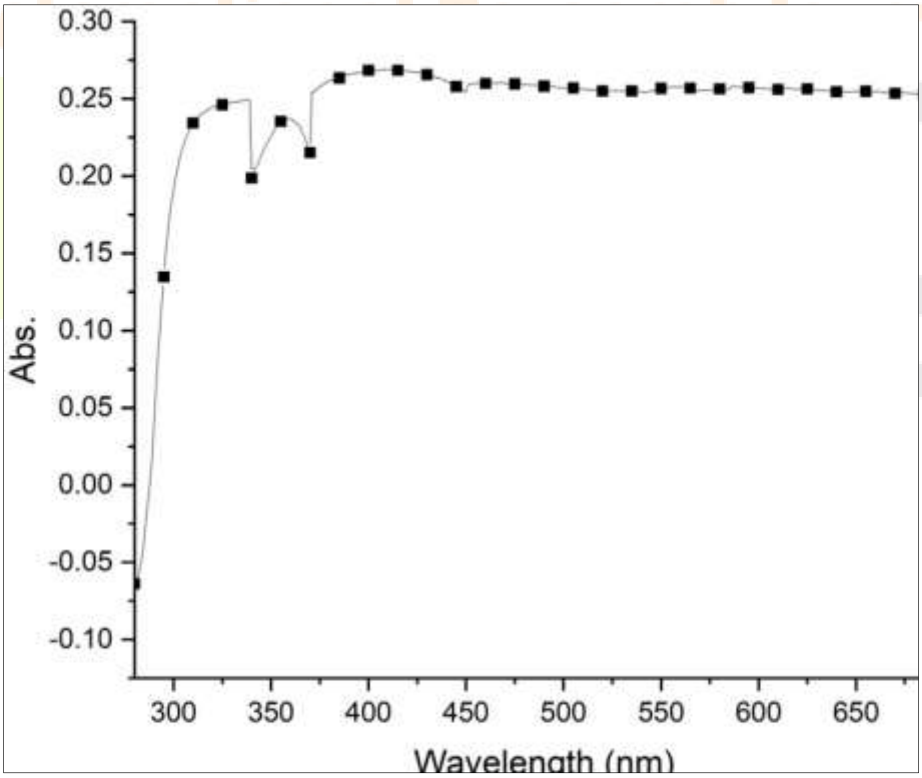


Figure 2: UV-visible spectrum of Zn-Cu nanoparticles

340 nm.

The figure 3 shows UV-visible spectrum of Zn-Fe-Cu NPs. It shows the peaks corresponding to all three metal nanoparticles.

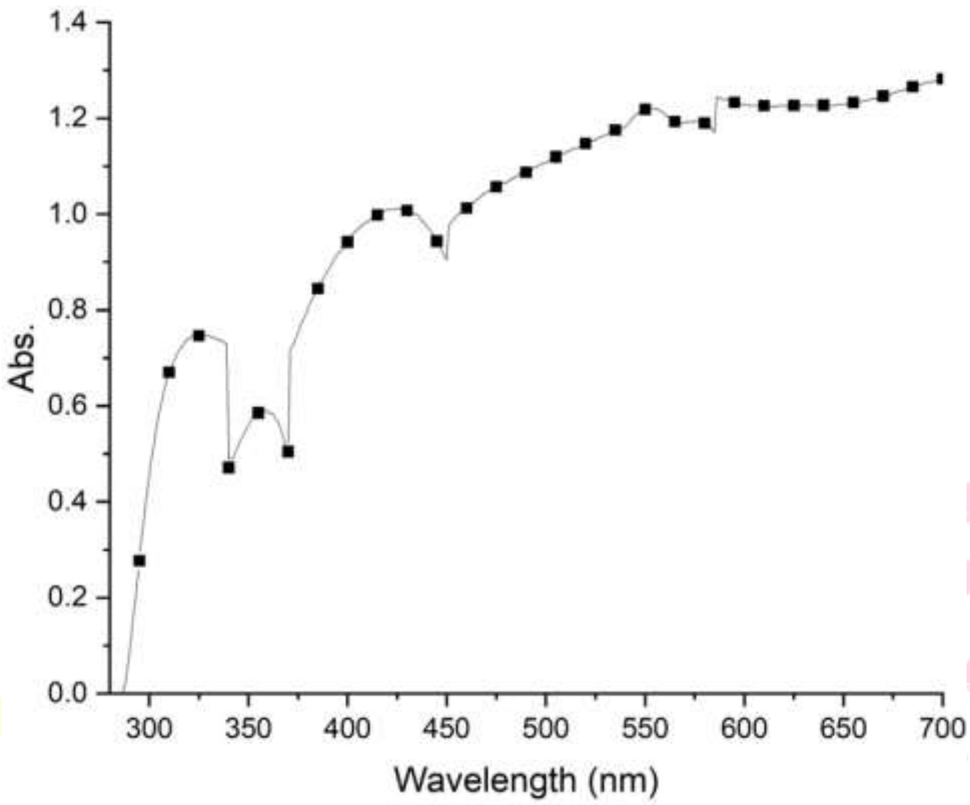


Figure 3: UV-Visible spectrum of Zn-Fe-Cu NPs

IR spectroscopy

IR spectra of all samples were obtained on IRTracer-100 SHIMADZU spectrometer. Figure 4 represents IR spectrum of Zn-Fe-Cu NPs.

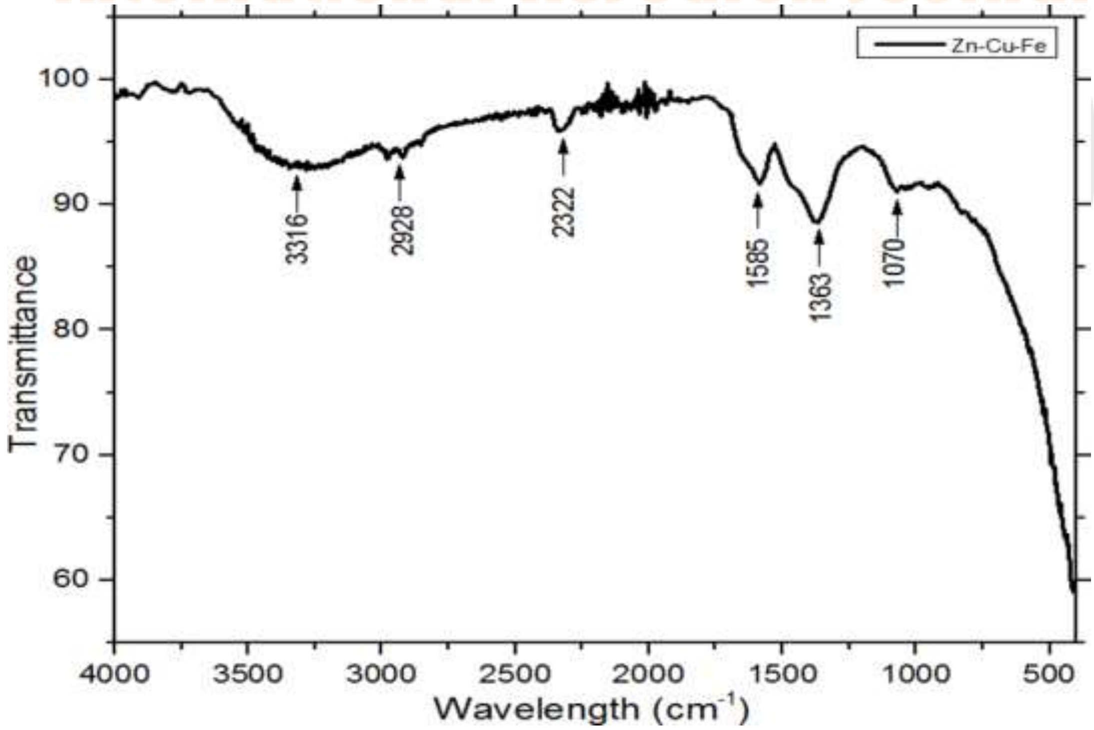


Figure 4: IR spectrum of Zn-Fe-Cu NPs

The peaks at 494 cm^{-1} is due to Zn–O bond's vibration. There were several minor peaks at 617.21 cm−1 and 580.00 cm−1 that might have been caused by the vibrations of the Fe-O, the peak at 697 cm−1 are

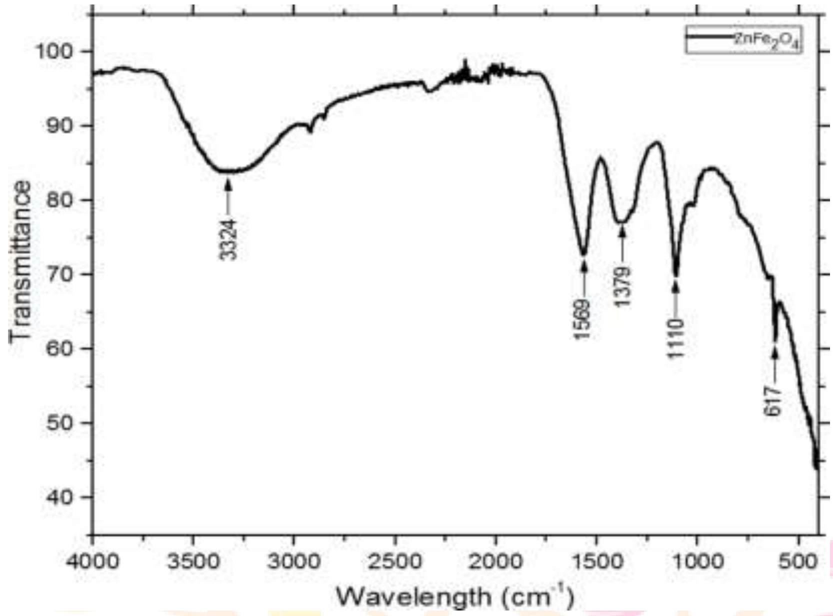


Figure 5: IR spectrum of Zn-Fe NPs

responsible for Cu-O bond.

The absorption maximum at 808.17 cm−1 is due to the bond vibration of aromatic C–H groups. According to the literature, the presence of aromatic ester or alkyl aryl ether in aqueous C–N bond vibrations and –C–O bond vibrations, which cause a number of additional peaks to arise at 1048.92 cm−1, 1070.37 cm−1, and 1110.02 cm−1.

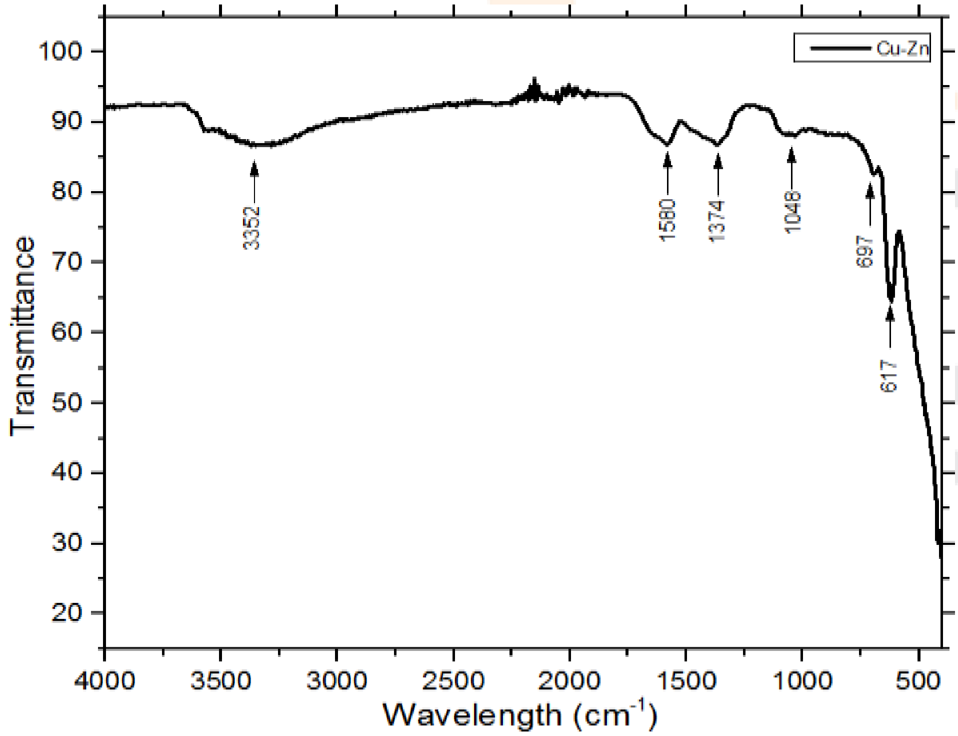


Figure 6: IR spectrum of Zn-Cu NPs

Due to the environment's absorption of CO2 and the asymmetric and symmetric modes of vibration of –C=O, O–C=O, and O–C–O, the monodentate metal carbonate (m-CO32−) appears to vibrate at 1379.96 cm−1, 1374.25 cm−1, 1363.76 cm−1, and1569.41 cm−1. The peaks at 1580 cm−1, 1585 cm−1, and 2322.37 cm−1 are caused by the water molecules' bending, as they are present on the surface of the synthetic material as a result of atmospheric adsorption. The bond vibrations of the C–H groups are said to be responsible for the peaks at 2928.43 cm−1 and 2926.01 cm−1. The broad peaks at 3324.36 cm−1 and 3316.48 cm−1 are connected to the OH group bond vibrations on the surface of the produced nanomaterials.

Dye Degradation study

In order to establish equilibrium, the wastewater treatment process was carried out in a three different beaker's containing 0.5 g/L of different nanoparticles, 100 mL of methylene orange dye aqueous solution, and 10 Moles of H_2O_2 in each beaker. The mixture was constantly stirred for 15 minutes. It was then exposed to direct sunlight for a duration of five hours.

Samples before degradation   After degradation

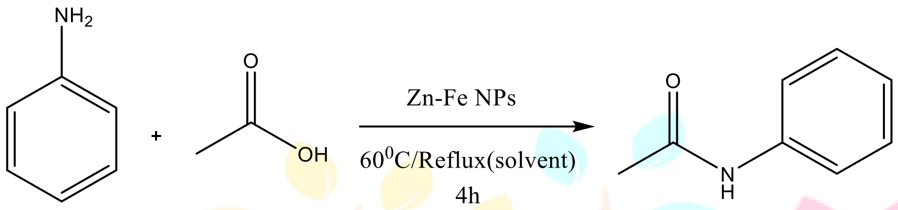
Figure 7: Samples before and after dye degradation study

The dye-degrading capacities of the three types of nanoparticles we used (Zn- Fe, Zn-Cu, and Zn-Fe-Cu) vary. The period of time it took for each combination of NPs to break down MO dye varied. There was a noticeable shift in solution color, which suggested that the dye was degrading. The Zn-Cu combination took a five hours solar irradiation and twelve hours to fully degrade the dye present (to become colorless) in the sample under study. The Zn-Fe-Cu combination took five hours of solar irradiation and ten hours in total to degrade the majority of the dye present in the sample water. The combination of Zn-Fe was also capable of degrade the dye, but it did so more slowly than the other two types of nanoparticles (20 hours). The degradation study was also carried out under concentrated solar radiation. The concentration of solar radiations was done by Fresnel lens. The assembly is shown in figure 8. But the results were not adequate as the sun rays were focused at a point and solution was not stirred. We hope better results with CSR following modified method.

Figure 8: Fresnel lens set-up for CSR

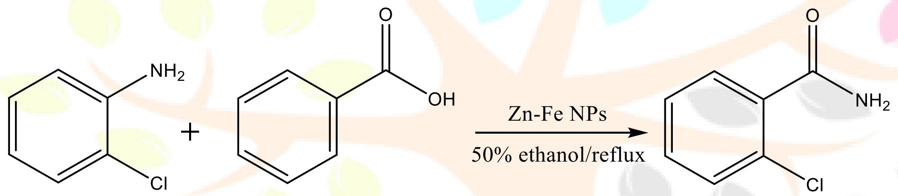
Catalytic activity study:

Zn-Fe nanoparticles' catalytic activity was investigated by employing them in a few reactions. The Zn-Fe nanoparticles were tested as catalyst in synthesis of acetanilide from aniline and acetic acid (Scheme 1). The solvent free and different solvent conditions were screened for the conversion. Solvents such as water, ethanol, and methanol were tested. The solvent free reaction was heated at 60 °C for four hours. In solvent study the reaction was refluxed for four hours. In ethanol and methanol, and acetanilide the expected results were not obtained; nevertheless, in water, a little conversion was seen on TLC, but we were unable to isolate the solid product. Reflux is used to carry out the reaction for four hours in the Zn-Fe nanoparticle-based synthesis utilizing 2-chloroaniline and benzoic acid in the presence of 50% ethanol and Zn-Fe nanoparticles as catalyst. The product's formation did not proceed as anticipated (Scheme 2).



Scheme 1: Study of catalytic activity of NPs synthesized

Without the use of a solvent, the synthesis of toluene from benzaldehyde utilizing Zn-Fe as a catalyst failed to produce the anticipated results.



Scheme 2: Amide formation reaction using Zn-Fe NPs

CONCLUSION:

Zn-Fe, Zn-Cu, and Zn-Fe-Cu nanoparticles were synthesized successfully by employing pomegranate peel extract. The colour changes and UV-visible and FT-IR spectral data suggest the formation of stable nanoparticles. These nanoparticles are stabilized, and reduced; and expected to be capped by the primary amines found in proteins and phenols. The dye degradation study advocates that the ZN-Fe-Cu nanoparticles are highly efficient as compared to two other NPs. Under solar radiation, the de-colorization efficiency for the elimination of methylene orange dye was examined and has future scope for better procedures. The methodology offers a cost-effective and environmentally friendly way to synthesize Zn-Fe, Zn-Cu, and Zn-Fe-Cu compounds. These are highly efficient in the elimination of methylene orange dye. In future scope, we believe, the employment the nano-composites in the water treatment plants, where they will be added to a feed bed column and then chlorinated to provide clean water for both industrial and residential use. Additionally, for future research, the usage of thus synthesized nanoparticles as catalysts in various reactions can be conducted under various reaction conditions to improve yield and promote green synthesis.

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