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Ultra-fast Photocatalytic Degradation of the Azo Dyes using Au/ZnO Nanocomposites

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Abstract

Water resource scarcity is increasing day by day, so effective treatment of wastewater is needed to grow water availability and the economy. Many wastewater treatment technologies have been developed, but nanomaterial sciences also play a vital role. So, in this study, a gold chloride zinc oxide (Au/ZnO) nanocomposite catalyst was synthesized using the chemical precipitation method. The degradation studies used methyl orange, eriochrome black tea, and bromocresol green as model dyes and textile industry wastewater. The nanocomposite was also characterized by various techniques such as FTIR, XRD, TEM, and Ultraviolet-visible spectrophotometer. The results represent that the FTIR spectrum of nanocomposites shows six-well peaks at different values, which signifies that N-H stretching primary amine, N-H stretching amine salt, O-H bending carboxylic acid, and C-I stretching are present in the nanocomposites structure. X-ray diffraction results show eight well-defined peaks at 2-theta, indicating the existence of a hexagonal-phase ZnO structure with Au. The transmission electron microscopy results show that Au is highly spread with a small size and uniform morphology over the surface of the ZnO. The UV-visible absorption spectra of nanocomposite samples showed a distinct band center around 350-400 nm. The concentration of 0.5 mL of 1.0 M sodium borohydride, methyl orange, eriochrome black tea, and bromocresolgreen, and five mg of the nanocomposite used in degradation studies, and the result was analyzed with the help of a UV-visible spectrophotometer. The average time of complete degradation was from five minutes to nine minutes. It was noticed that the prepared Au/ZnO nanocomposite is very effective and eco-friendly for the degradation of dyes and wastewater.

Keywords: Au/ZnO Nanocomposites, Organic Azo Dyes, Photocatalytic, Degradation, Methyl Orange, Eriochrome Black T, Bromocresol Green

1. Introduction:

Nanotechnology is broadly used in numerous fields, suchas agriculture, foodindustries, biotechnology, and medicine. It can be defined as the field of applied science and technology based on controlling matter on the atomic and molecular scaleinthe1-100 nm range and the fabrication of devices with critical dimension slying in this range [1]. Metal nanoparticles such asgold, silver, and copper display unique electronic, optical, and catalytic properties [2, 3]. Gold nanoparticles (AuNPs) have gained increasing attention with special features [4, 5]. Organic dyes are widely used in various industries, including paper and pulp, textiles, pharmaceuticals, and dye intermediates, as well as in tannery and Kraft bleaching processes. When these dyes are discharged into natural water resources, they generate organic pollutants. The textile industry, in particular, is a major contributor to this pollution, utilizing around 1,000 different dyes [6-8]. It is estimated that the annual global production of these dyes is 7.105 metric

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tonnes. About 30% of these dyes are produced at a rate of over 1,000 tonnes per year, and 30% are used at the level of 100 tonnes per year. During the dyeing process, 90% of textile products are treated with dyes, with approximately 10-25% of the dyes lost in the process and 2-20% discharged directly into the environment. It is also estimated that 50% of the dyes are azo dyes, characterized by their nitrogen double bonds (N=N) [9-11].

Many researchers are working on wastewater, which is polluted by direct or indirect discharge of toxic substances from different sources, but textile industry dyes are the main source of water pollution because industrial and textile dyes have organic compounds that create about 70000 tonnes per year [12-14]. Now day, worldwide water pollution is one of the most severe problems because the population is increasing, and consumption of water also increases continuously in industries and domestic sectors; about 70, 22, and 8% of the existing fresh water is used by the sesectors. Due to the huge quantity of water used in industries, a large quantity of wastewater is generated, which contains many pollutants. The quality of drinking water is a critical issue in this domain, and drinking water pollution is one of the primary environmental issues that affect human health worldwide [15]. The World Health Organization (WHO) considers that organic dyes signify the main challenges in the delivery of safe drinking water. There are various traditional methods have been developed to remove these organic dyes from the wastewater, such as activated carbon, adsorption, flocculation, coagulation, and reverse osmosis; they are not so effective as compared to the advanced oxidation process [16-18].

The people of our country, especially poor folks, are being faced with intense health problems, which are further increased due to the lack of resources and hence, no proper toxic wastewater treatments. The organic dyes are mostly aromatics in structure and have a synthetic nature; due to this, these are non-biodegradable and cause allergies and skin irritants that have carcinogenic action, which is expressed both chronically and acutely [19]. Azodyes havea high potential risk to human health, and their breakdown causes the formation of toxic products in the gastrointestinal tract, lungs, and skin, as well as the disruption of blood. Organic dyes have a high number of aromatic molecules, which is why biological methods such as decolorization and degradation cannot be removed easily from these organic dyes, and some physical methods such as activated carbon, coagulation, and reverse osmosis are very costly. Moreover, these methods don't quickly degrade the dye; just change its phase [20, 21].

In this research work, the fabricated composite nanomaterial of Au/ZnO is used to remove the organic azo dyes from industries' wastewater using ultra-fast photocatalyst degradation composites. It is also important to have a good dispersion and robust photocatalyst materials that could not only increase the adsorption ability but also the resistance of the NCsM/MO. Nowadays, a new method, such as the advanced oxidation process (AOPs) based on photocatalysts, is more effective and has been developed to remove these organic dyes from the wastewater. The benefits of this method are the mineralization of organic compounds, no wastewater problems, and mild pressure and temperature processing [22, 23]. The fabricated photo catalyst in this research will have several commercial applications as compared to other treatment methods.

2. Experimental section:

2.1. Chemical and reagents:

For the synthesis of nanocomposites, some chemicals are used, such as gold chloride (AuCl), zinc acetate dihydrate $(CH_3\ COO)_{2.Zn.2H2O}$), sodium citrate ($C_6H_5NaO_7.2H_2O$) and sodium hydroxide (NaOH). All chemicals were purchased from Sigma Aldrich, and sodium citrate is used as a capping and reducing agent, as well as sodium hydroxide, to increase the rate of reaction. For the degradation, we use some dyes such as methyl orange ($C_{14}H_{14}N_3NaO_3S$) eriochrome black T ($C_{20}H_{12}N_3NaO_7S$), bromocresol green ($C_{21}H_{14}Br_4O_5S$) from Sigma Aldrich were purchased.

2.2. Cleaning of glassware:

All the glassware, such as beakers, conical flasks, volumetric flasks, and micropipettes, was cleaned with a detergent solution using tap water; after that, the glassware was kept overnight in 2 M of 60% of HNO_3 that can soak water that was again washed with distilled water many times then ethanol also used to all glassware to remove organic and in organic impurities.

2.3. Site selection:

Kotri is the 29th largest city in Pakistan; it is in Jamshoro district and it is situated on the right side of the Indus, It has a population of 259358 as per CENSUS 2017. There are many industries in Kotri, and textile industries produce large amounts of wastewater, which affects the environment and human lives. So, the sample of wastewater was collected from dye discharge effluent of textile mills (Kotri) Sindh, Pakistan, as mentioned in Fig.1.

Figure 1: Map for sampling from textile industry Kotri.

2.4. Wastewater sampling protocol:

The wastewater sample was collected from discharge effluent of textile mills (Kotri); only one sample was collected in a 1-liter bottle, and itwas used for degradation.

Following some are protocols that are used during the study

1. Wore gloves and masks
2. keep sample ID on the bottles
3. Open the faucet for one minute before collecting water so that the water can run
4. After filling the bottle, it was capped and kept in an ice box for transportation

2.5. Sample collection and transportation:

The sample was collected from textile mills Kotri in an autoclave plastic bottle of 1 liter and placed in an ice box; then,the sample was transported to the US-Pakistan Center for Advanced Studies in Water (USPCASW), MUET Jamshoro.

2.6. Synthesis of Au/ZnO nanocomposite photocatalyst:

The Au/ZnOnanocomposite was prepared by the precipitation method; in this process, the stock solution of 100 mL was prepared,zinc acetate 0.5 M in 50 mL,sodium citrate 1.0 M in 50 mLthis chemical was used as a reducing agent, and sodium hydroxide1M in 30 mL it is used to active the reaction. Initially, in a 500 mL beaker gold chloride 10 mL, 40 mL distilled water, zinc acetate10 mL, sodium citrate 10 mL were mixed and slightly heated stirrer for 5 minutes; after that,10mL of sodium hydroxide was added suddenly,the color changed from white to white milky (precipitated) as shown in Fig.2. After that the sample was filtered and put in the oven at a temperature of 50 ^{o}C for 30 minutes. Then, it is used to degrade dyes through UV-Vis spectroscopy.

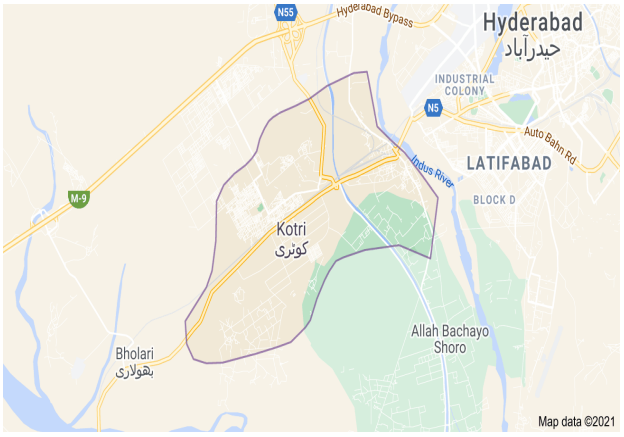

Figure 2: Solid precipitate of Au/ZnO nanocomposite.

2.7. Characterization of Au/ZnO photocatalyst:

In this step, we optimization of various parameters such as concentration of capping agent, metal solution, pH, temperature, reaction time,etc., would be done to get the smallest possible particles with mono-disperse behavior and characterization for synthesis of M/MONCs photocatalyst by various techniques such as UV-Vis, FTIR, SEM, TEM, XRD and other advanced techniques for morphological determination. From these results, the data will be analyzed and compared in terms of particle size, elemental composition, and phase segregation.

2.8. Photocatalytic application activity of Au/ZnO M/MO NCs:

In this step, the developed NCs were applied to some selected dyes such as methyl orange, erichrome black tea, and bromocresol green;after that, the sampleswere collectedfromdyesdischargeeffluent(wastewater)fromsit eareasofKotritextiledyes industries, Sindh Pakistan. The synthesized photocatalytic activity of NCs M/MO would be applied to the degradation of organic azo (Nitrogen-containing aromatic compounds) toxic dye effluent from wastewater samples. Thephotocatalytic activity of the

nano-catalyst will be evaluated by measuring the decomposition of the distilled water solution of organic azo dyes; the organic azo pollutants degradation will be monitored by UV-visible spectrophotometer

2.8.1. Preparation of solutions of dyes:

Methyl orange, eriochrome black tea, and bromo cresol green. The all-dyes solution of 0.1M in 50mL was prepared, and 0.001 M in 50 mL of sodium borohydride was also prepared. The mixture of these three dyes also degraded.

2.8.2. Degradation of Methyl Orange:

The degradation of methyl orange dye was performed with the help of a UV-visible spectrometer in a scanning program at the wavelength of 300 to 700nm. Initially, 100µm of methyl orange was taken from the solution and put into cubits,then the scanning program, that 30µm of sodium borohydridewas added, and again scanning started.Finally, 4mg of the developed nanocompositewasadded and startedscanning till complete reduction of methyl orange and time were noted.

2.8.3. Degradation of Eriochrome Black-T:

The Degradation of Eriochrome black-T dye was performed with the help of a UV-visible spectrometer in a scanning program at the wavelength of 300 to 700nm. Initially, 100µm of Eriochrome black T was taken from the solution and put into UV cuvettes,then the scanning program; after that, 30µm of sodium borohydridewas added,and again scanning started. Finally,5mg of the developed nanocompositewas added and started scanning till complete reduction of Eriochrome black T and time were noted.

2.8.4. Degradation of Bromocresol Green:

The Degradation of Bromocresol green dye was performed with the help of aUV-visible spectrometer in a scanning program at the wavelength of 300 to 700nm. Initially, 100µm of bromocresol green was taken from the solution and put into cuvettes, then the scanning program; after that, 30µm of sodium borohydride was added, and again, finally, 4mg of the developed nanocomposite was added and scanned till complete reduction of bromocresol green and time were noted

2.8.5. Degradation of a mixture of dyes:

The degradation of a mixture of three dyes was performed by a UV-visible spectrometer ina scanning program at the wavelength of 300 to 700.When 10 mL of each dye was mixed with each other,100 µmof themixture of dyes was taken from it and put into cuvettes;then the scanning program and also 30 µmof sodium borohydridewere added,and thescanning program run. Finally, 5mg of thenanocompositewas added into cuvettes,and again, thescanning program started till thecomplete degradation of three dyes and time were noticed.

2.8.6. Preparation of syntheticsolutions of wastewater:

The prepared nanocomposite used for the different concentrations of wastewater such as(10ppm,1 ppm, 0.5ppm, and 0.1ppm) for the further work experience has been done through this process,and the formula used for dilution, which is given below

$$V2 = (C1*V1)/ C2 \ldots\ldots\ldots\ldots (1)$$

2.8.7. Effect of nanocomposite doses:

The different doses of nanocomposite used for the degradation of dyes and wastewater in the textile industry are 2mg, 3mg, and 5mg. The nanocomposite was added to different concentrations of wastewater, and the degradation of dyes was measured using UV-visible spectroscopy.

The number of dyes adsorb on nanocomposite at time "t"was acquired by the following Equations

$Qt=(C0-Ct) * v/ m \ldots\ldots\ldots\ldots\ldots(2)$

Were

qt =the amount of nanocomposite in mg is adsorb on adsorbent in gram at time t

C0 = concentration initially of nanocomposite (mgl^{-1})

Ct =concentration of adsorbent at time t (mgl^{-1})

v = amount of solution (mL)

m = adsorbent mass (mg)

Removal efficiency in percentage = $(C_0 - C_t) / C_0 * 100$

2.8.8.Degradation of wastewater in the textile industry:

The sample of wastewater from the textile industry was collected from Kotri, Hyderabad, Sindh. It is also used for degradation, which is performed by a UV-visible spectrometer in a scanning program at a wavelength of 300 to 700. Initially, 100 µm of wastewater with different concentrations was taken and diluted with DI water, then put into cubits, and the scanning program;after that,5mg of nanocomposites were added, and the scanning program completedthe degradation of wastewater of the textile industry and time was noticed.

3. Results and discussion:

3.1. UV-visible study:

The UV-visible spectra analysis was used to find the

absorption band of the nanocomposite at the wavelength of 200-700 nm. After that UV-visible spectra analysis, the result shows a strong spectra band in the range of 350- 400nm, which is shown in Fig. 3. From the literature, we find that the results of UV-Vis spectra analysis are nearly the same as described in the spectra expression that the sharp peak of in the UV region is around 350 nm for the prepared Au-ZnO photo catalysts. In this case, the UV- Vis spectra of Au-ZnO show a visible substantial absorption in the 200–700nm wavelength range. The cause of the absorbance in the visible range can be referred to as the fact of lowering of the band gap because of the accessory of the Au nanoparticles on the surface of the ZnO; the rise in absorbance is also accredited to the fact that the Au cylindrical nano rods cover further surface area of the ZnO spheres and have more area in the connection interfaces.

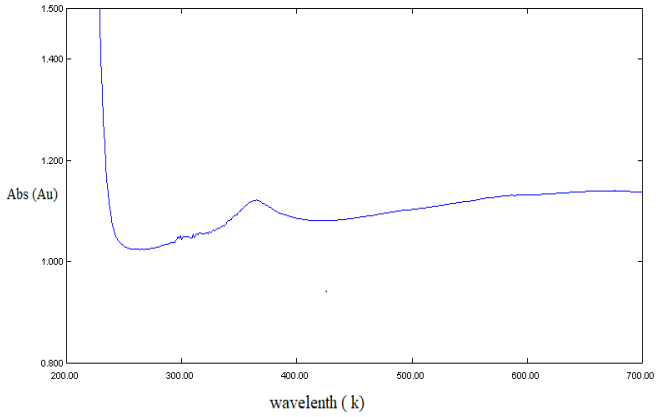

Figure 3: UV-Visible spectra of Au/ZnO nanocomposite.

3.2. FTIR study:

FT-IR spectroscopy was used to get information regarding chemical changes in the function groups involved in the Au/ZnOnanocomposites. The FTIR spectrum of Au/ZnOnanocomposites shows six peaks at 3432, 2926, 1434, 883, 724, 580 cm^{-1}as shown in Fig. 4. The peaks at 3443cm^{-1}show N-H stretching primary amine and also peak at 2926cm^{-1} shows N-H stretching amine salt, peak at 1434cm^{-1} show O-H bending carboxylic acid, the peaks at 883 and 724cm^{-1} shows C-C bending alkaline, finely at the peak 580cm^{-1} shows C-I stretching.

3.3. XRD study:

The XRD analysis is used for the study of the crystalline structure of Au/ZnOnanocomposites and the XRD spectra of nanocomposites shows eight fine determined peaks at 2θ°corresponding to 29.60°, 31.65°, 34.39°, 36.48°, 48.18°, 56.77°, 62.62°, and 68.10° and lattice planes is (100),(002),(101),(111),(200),(110),(112) and (004), correspondingly as represented in Fig. 5. The XRD pattern of peaks shows hexagonal phase ZnO structure with Au of the nanocomposites structure and the result also shows that the all peaks of XRD pattern have good arrangement with ZnO and Au as described in JCDPS card no 36-1451 and 04-0784 respectively.

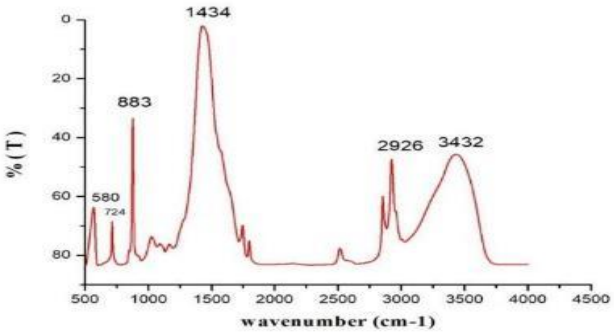

Figure 4: FTIR spectra of Au/ZnO nanocomposite

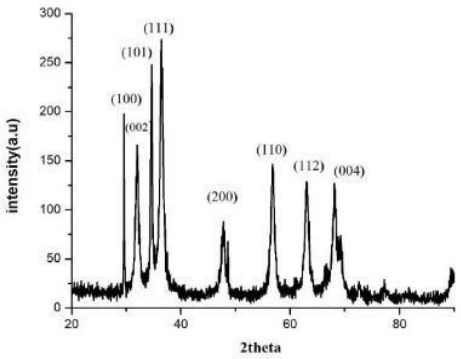

Figure 5: XRD pattern of Au/ZnO nanocomposite.

3.3.1. Calculating D-spacing of XRD:

We can calculate d-spacing from the XRD data by using Bragg's law equation [24], which is given below

$$n\lambda = 2dsin\theta$$

Or

$$d = \frac{n\lambda}{2dsin\theta}$$

Where

λ = 1.5406A° (Wave Number of Incident X-Ray)

n = 1st order of diffraction

θ = is the Braggs angle of diffraction

d = inter-planar spacing

The D-spacing was calculated from the XRD data with the help of origin software,and data was calculated in Excel by using Braggs law,as shown in Table 1.

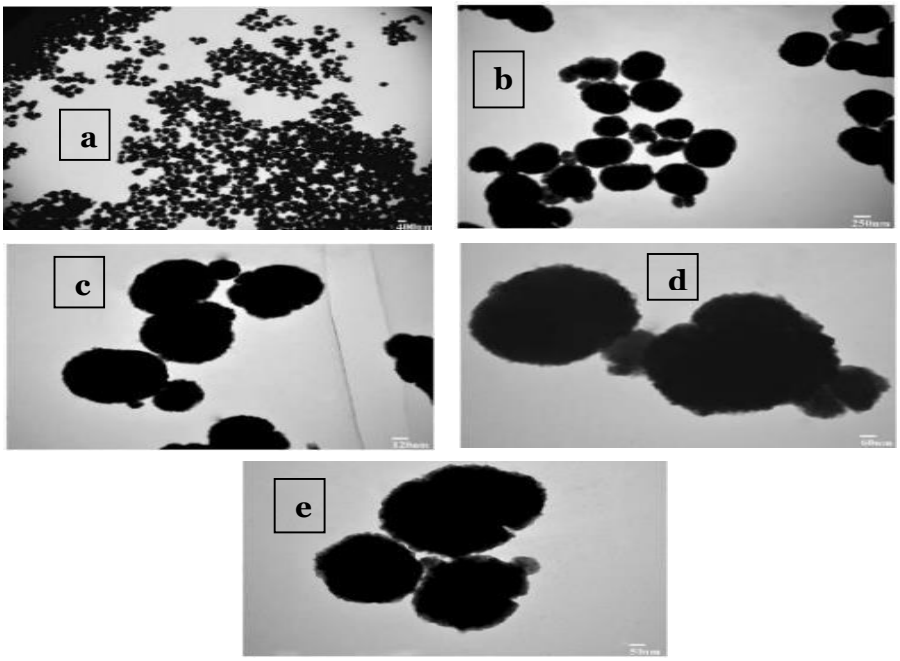

Figure 6: TEM images (a-e) from different magnification of Au/ZnO nanocomposite

Table 1:2θ and d-spacing values of the (111) diffraction peak by XRD of Au/ZnO nanocomposites

2Ɵ	Ɵ	d-spacing values (nm)
29.60592	14.80296	**3.0137493**
32.00415	16.00208	**2.7931728**
34.62918	17.31459	**2.5872092**
36.46465	18.23233	**2.4610796**
47.79363	23.89682	**1.9008086**
56.7948	28.3974	**1.619061**
63.02647	31.51324	**1.473133**
68.27782	34.13891	**1.3720569**

3.3.2. Calculating particle size:

Calculating nanocomposite size from the XRD data, I select plane (111) to get the value of FWHM using the Scherrer equation with the help of the origin software.

$$D = \frac{0.89\,\lambda}{\beta cos\theta}$$

Where

0.89 → is Scherrer constant value

λ = 1.5406A° (X-ray wavelength)

β = FWHM (Full Width at Half Maximum)

So, we select peak or plane number (111) and get the value of FWHM by the help of origin and put in an equation

$$D = \frac{0.89*1.5406}{0.79129*cos(36.48)}$$

D = 2.03 nm

Using thesame formula,just theconstant value changed

$$D = \frac{0.9\,\lambda}{\beta cos\theta}$$

By putting all values in theequation, we get

D = 2.06 nm

3.4. TEM analysis:

The application of TEM in nanoscience is very momentous in viewing the nanocomposites innanoscale size. The given TEM images at different magnifications of synthesized Au/ZnOnanocompositeare shown in Fig. 6 (a-e), which clearly indicates the size, shape, and size distribution of nanocomposites.

3.4.1. Core-shell of nanocomposites:

Thegiven image is the core-shell of the nanocomposite,which shows that the three good SEAD patterns and structure of nanocomposite are polycrystalline, as shown in Fig. 7.

3.4.2. Histogram:

The size distribution histogram of Au/ZnOnanocompositewas performed by using ImageJ software and Origin Pro, as shown in Fig. 7. The results show that the minimum size of nanocomposite is 221

nm and the maximum size of nanocomposite is 646 nm

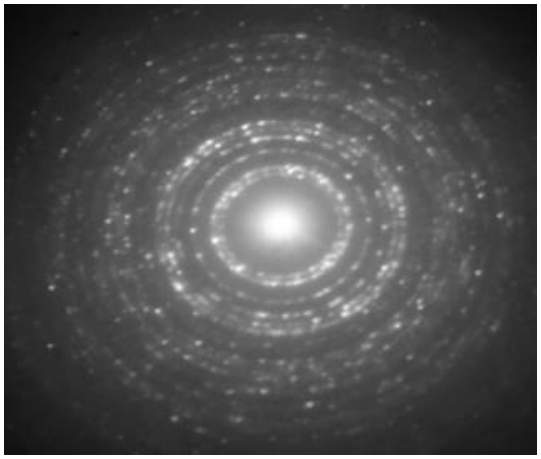

Figure 7: SEAD patterns of Au/ZnO nanocomposite.

and also it shows that Au is highly spread with small size and uniform morphology over the surface of the ZnO as shown in Fig. 8 and Table 2.

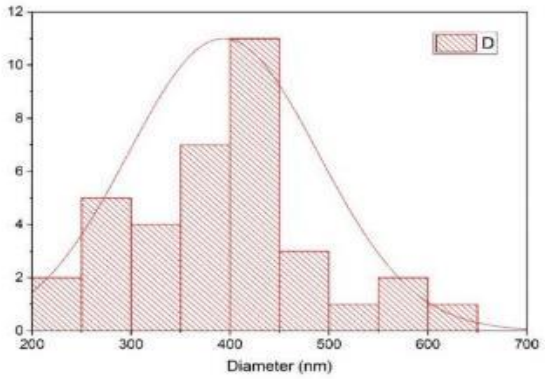

Figure 8: Size distribution histogram of Au/ZnO nanocomposite.

Table 2: Statistical data for particle size distribution (minimum & maximum) of Au/ZnO NCs

	N total	Mean	Std. Dev.	Sum	Min.	Median	Max.
D	36	393.28	96.096	14158.08	221.939	400.1	646.251

3.5. Application Study:

3.5.1. Degradation of methyl orange dye:

The results from the degradation of methyl orange initially, the absorbance of methyl orange is about 0.9; when $NaBH_4$ was used, the reduction occurred to 0.72 but the reduction rate was very slow after that when Au@ZnO NCs used the reduction rate was very fast and it degraded the methyl orange from 0.72 to 0.54 as shown in Fig. 9. During the degradation process, the absorbance decreases again to 0.21 and final absorbance was 0.04.The time was noticed, and the whole reduction was completed within 6 minutes, and the color of methyl orange was changed to colorless.

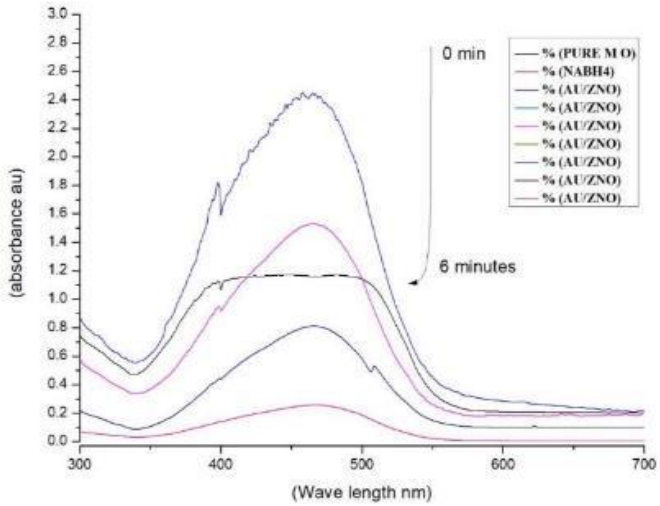

Figure 9: UV–visible spectral changes for photo degradation of Methyl orange under UV light irradiation with Au/ZnO nanocomposites.

3.5.2. Degradation of Eriochrome black-T dye:

Figure 10 shows the degradation of eriochrome Black T in which the initial absorbance of EBT was about 0.16 when $NaBH_4$ used absorbance decrease to 0.1 and thenAu@ZnOnanocompositesused the absorbance decrease to 0.7, 0.5, 0.4 and final absorbance is 0.2 the whole reduction process takes 5 minutes to complete the Degradation of EBT and finally the color of EBT changed to colorless.

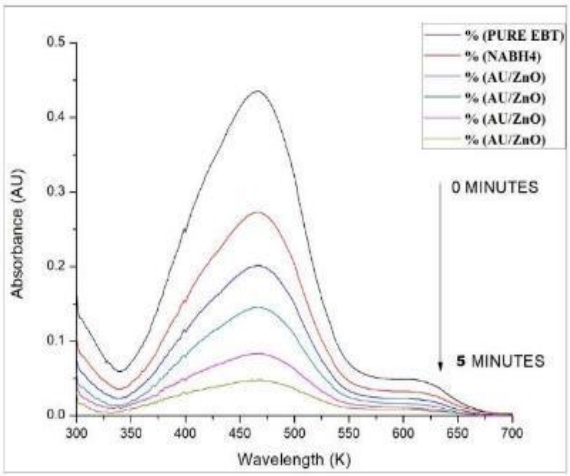

Figure 10: UV–visible spectral changes for photodegradation of EBT under UV light irradiation with Au/ZnO nanocomposites.

3.5.3. degradation of bromocresol green dye:

Figure 11 signifies the degradation of bromocresol green dye;the initial absorbance is about 0.2, but when $NaBH_4$was used, it decreased to 0.19 after that,Au@ZnOnanocomposite used for further degradation, and the absorbance decreased from 0.19 to 0.16 than 0.1,0.04,0.03, and final absorbance is 0.02. The time was noticed,and within five minutes, the reduction was completed, and the color of the dye changed to colorless.

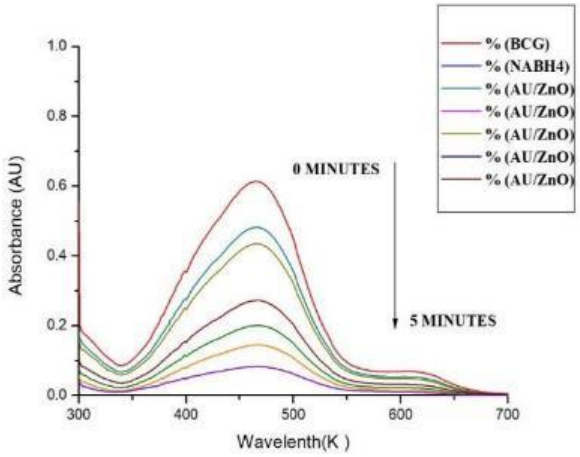

Figure 11: UV–visible spectral changes for photodegradation of BCG under UV light irradiation with Au/ZnO nanocomposites.

3.5.4. Degradation of three mixtures of dyes:

Figure 12explains the results of the mixture of three dyes in which the original absorbance of the mixture dyes is about 0.35,and by using sodium borohydride, the absorbance declines from 0.35 to 0.2. Subsequently, Au/ZnONanocompositeswere used for degradation, and they reduced absorbance to 0.18,0.1,0.04, and the final absorbance was 0.03; the degradation procedure took 8 minutes to complete, and the color of dyes changed to colorless.

3.5.5. Effect of nanocomposite adsorbent doses:

The adsorption of dyes on nanocompositeisinfluenced by the adsorbent dose and the effect of the dose of nanocomposite. The removal percentage caused by the dose of Au@ZnOnanocomposite of equilibrium concentration increased by increasing the dose of nanocomposite from 2mg to 5mg. The removal of dyes from wastewater increased from 95.5% to 99.7%,as shown in Fig. 13.The highest removal efficiency was

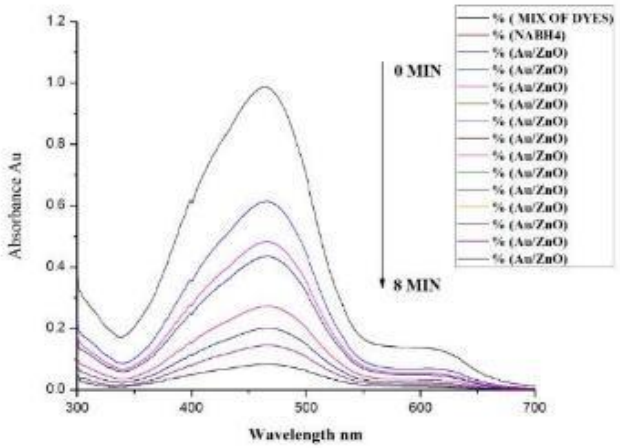

Figure 12: UV–visible spectral changes for photodegradation of a mixture of three dyes (MO + EBT + BCG) under UV light irradiation with Au/ZnO nanocomposites.

achieved when the maximum dose of adsorbent was added due to theavailability of maximum vacant spaces present on the surface of the adsorbent the quantity of adsorbent used in an experiment is directly proportional to the number of sites available for adsorption [25].

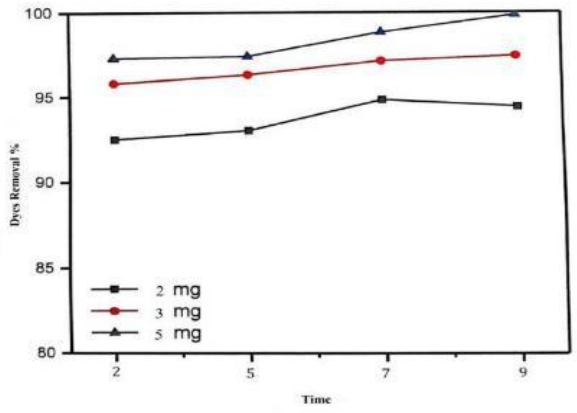

Figure 13: Effect of adsorbent dose (Au/ZnO nanocomposites) on the removal of organic dyes.

3.7. Degradation of textile wastewater:

Figure 14 represents the results of the degradation of organic dyes from textile industry wastewater. The original wastewater absorbance is 3.25 when Au/ZnOnanocomposites used for degradation of wastewater absorbance decreaseto 1.51, 0.8, 0.7, 0.04,

0.03, and the final absorbance is 0.01. The degradation procedure takes 9 minutes to complete, and the color of the wastewater is changed to colorless.

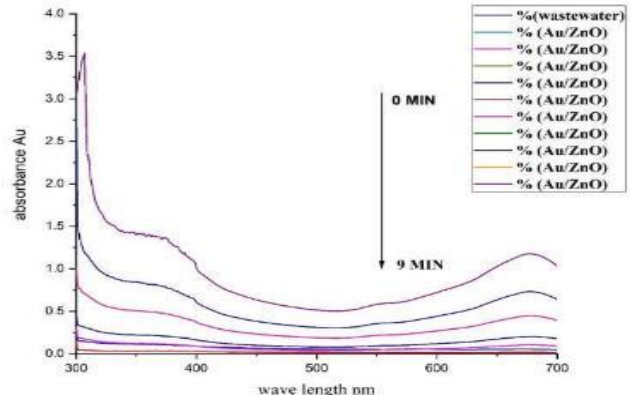

Figure 14: Degradation of organic dyes (MO + EBT + BCG) from real wastewater sample from the Kotri textile industry.

4. Conclusions:

A novel Au/ZnO nanocomposite was successfully synthesized using a chemical precipitation method. Characterization techniques such as XRD, FTIR, TEM, and UV-visible spectroscopy confirmed its structure and composition. XRD analysis revealed a hexagonal wurtzite ZnO structure, with successful incorporation of Au nanoparticles. FTIR identified functional groups like N-H, O-H, and C-C, which can enhance interactions with organic pollutants. TEM images showed a uniform distribution of Au on ZnO, with particle sizes ranging from 221 to 646 nm, indicating a well-dispersed nanocomposite. UV-visible spectra exhibited a strong absorption band at 350-400 nm, corresponding to ZnO's characteristic absorption, enabling efficient light absorption for photocatalytic reactions. This nanocomposite demonstrated remarkable efficiency in degrading dyes such as methyl orange, EBT, and bromocresol green, as well as textile wastewater, within minutes. Its high photocatalytic activity is attributed to enhanced light absorption and efficient charge separation, facilitated by the Au/ZnO interface. The successful synthesis and high degradation efficiency make the Au/ZnO nanocomposite a promising candidate for wastewater treatment applications, particularly in regions like Pakistan, where textile effluent poses a significant environmental challenge.

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