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Monodispersed Gold Nanoparticles within PVA Film for Efficient Catalytic Degradation of Methylene Blue.

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ABSTRACT

Polyvinyl Alcohol (PVA)/gold (Au) nanocomposite was prepared via seeded-growth route. The nanocomposite was characterized using UV-vis spectrophotometer, X-ray diffraction (XRD) and Transmission electron microscope (TEM). The application of PVA/Au as a catalyst for methylene blue (MB) dye degradation in water was investigated. The ability of reusing such nanocomposites as well as the effect initial dye concentration on the catalytic process was evaluated.
Keywords: monodispersed, gold nanoparticles, PVA, methylene blue.

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INTRODUCTION

Many industries such as chemicals, textile, refineries, leather, paper, and plastic, use different types of dye kits in various processing steps. The concentration of the dyestuffs in the wastewaters is variable depending upon the type of industry [1]. Generally, 30–40% of these dyes remain in the waste waters coming from these industries. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life. Remediation of wastewaters containing these pollutants is very difficult due to higher solubility and resistance to biological degradation [2]. Many processes have been developed for phenolic compounds removal such as adsorption, microbial degradation, photocatalytic degradation, electrocoagulation and electrochemical treatment and so on [3].

In recent years, nanophase materials have gained more attention because of special physical and chemical features. Gold nanoparticles (Au NPs) attract a great deal of interest due to its well-known catalytic activity, optical properties and chemical functionability. It can catalyze many reduction reactions [4]. Reductive degradation of pollutants using zerovalent Au NPs inspire researchers due to many benefits such as high rate of reaction and efficiency, non-toxicity, insolubility, mild reaction conditions, and requirement for minimal follow-up treatment. However the use of Au NPs as a catalyst faces many difficults such as mass transport, and possible environmental and health risks caused by the potential release of nanoparticles into the environment [5]. One of the limiting factors that hinder the practical use of soluble Au NP catalysts is the difficulty in recycling and reusing them [6]. Consequently the development of new Au NP systems that can be used in a facile fashion is desirable.

In the present work, it was attempted to establish the degradation pathway of a dye present in colored aqueous effluents from textile industries. The model dye chosen was methylene blue (MB). Methylene blue (MB) is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturition, and methemoglobinemia like syndromes [7]. Therefore, removal of Methylene blue from wastewater is most desirable.

MATERIALS AND METHODS

Materials

Chloroauric acid ($HAuCl_4 \cdot 3H_2O$) was obtained from Sigma–Aldrich Co. Sodium borohydride ($NaBH_4$) was purchased from Merck Co. Polyvinyl alcohol with an average molecular weight of 14,000 g/mol was obtained from Laboratory Rasayan, India. It was in the form of powder, partially hydrolyzed and used without further purification. All reagents were of analytical grade and used without further purification. Methylene Blue (MB) was purchased from Merck Co. with molecular weight 355.89 g/mol.
All solutions were prepared using deionized water.

Preparation of the PVA/Au nanocomposites

In a typical preparation procedure, dissolve 3 g of PVA in 50 mL of deionized water at 90 ^{o} C with magnetic stirring for about 10 h until clear solution is obtained. The solution is left to cool at the ambient condition. Then 0.5 ml of 0.025 M $HAuCl_4$ was added to 5 ml of PVA solution with continuous well stirring for about 2 h. Thereafter, 250 μ of 0.1 M $AgNO_3$ were added to the above mixture. The pH value of the solution was adjusted to 4 with an aqueous solution of 0.1 M HCl. Finally, the solution was casted on a Petridish, left to dry in darkness to form the desired film and then the film was stripped from the dish. The film's thickness was controlled with the casting condition, i.e. the volume of the casted mixture and the size of the Petri dish were kept constant. The color of the casted film was faint yellow. Photoreduction of PVA/Au film was carried out using VilberLourmat Lamp, SVL, France at wavelength 254 nm at ambient conditions. The UV illumination time was 4 h at 10 cm distance.

Analysis techniques

Optical absorption spectra of the PVA/Au nanocomposite films were recorded in the spectral range 200–1000 nm using a PG Instruments T80+ UV–visible double-beam spectrophotometer (PG Instruments, United Kingdom). The crystalline and phase structures were determined by using X-ray diffraction XRD-DI series, Shimadzu apparatus using nickel-filter and Cu–K target (k = 1.5406 Å). The shape and particle size distribution were studied using JEOL JEM 2010 Transmission Electron Microscope operated at 100 kV accelerating voltage.

Catalytic degradation of MB

In a typical experiment, 1ml of $NaBH_4$ (0.1 M) was added to 20 mL of MB (2.8×10^{-3} M) aqueous solution under stirring. Apiece of nanocomposite film (0.0728 gm) was taken into the solution. Thereafter, the degradation of MB was monitored through vanishing of the absorption peak at 690 nm recorded by the successive UV–visible spectra.

RESULTS AND DISCUSSION

Visual inspection

The reduction of gold ions within PVA matrix into gold nanoparticles was visually identified by color change from yellow to dark pink. Generally, gold ion exhibits yellow color in distilled water. It was observed that the color of g1 sample is still yellow as that of gold ions. This means that the gold ions were not reduced under these condition i.e. the presence of HCl prevent the spontaneous reduction of gold ions. The UV-irradiation of sample g2 shows a pale pink color after 4 h which indicates the reduction of gold ions into gold nanoparticles. Quite interestingly, the g3 sample respond more quickly to the UV-irradiation thereby observing the fast color change of this sample.

UV–visible absorption studies

Au NPs show a strong absorption band in the visible region when the frequency of the electromagnetic field is resonant with the coherent electron motion, which is called surface plasmon resonance (SPR) absorption [8]. Well established theoretical models allow correlating the optical absorption spectra both to the morphological and topological structure of nanoparticle systems dispersed into a homogeneous dielectric medium. Peak position, shape, FWHM and maximum value of the absorption spectrum are related to the shape, diameter and composition of clusters system. Thus, the analysis of the plasmon absorption peak provides information about the quality of the prepared samples (particle size, size distribution and the amount of reduced gold nanoparticles) [9,10].

Figure 1 show the UV–visible absorption spectra of the three samples under investigation. The spectrum of g1 sample show nearly zero absorption in the wavelength range (1000-470) nm followed by absorption enhancement extended from 470 nm to the UV regions. The absence of the SPR band confirms that the acidification with HCl success in preventing the spontaneous reduction of Au^{3+} with PVA.

Alternatively, a broad SPR band was observed at 530 nm on the spectrum of g2 sample. The UV-visible results proved that, the Au nanoparticles could be synthesized from the PVA film filled with $HAuCl_4$ in solid phase with the UV-irradiation. The SPR band of gold nanoparticles is broad with an absorption tail in the longer wavelength that extends well into the near-infrared region attributing the excitation of the in-plane SPR and indicates considerable anisotropy in the shape of Au nanoparticles. This could be in practice due to the size distribution of the particles [11].

Upon the addition of $AgNO_3$ to PVA/$HAuCl_4$ (sample g3), an interesting feature was observed. An intense and narrow SPR of spherical Au nanoparticles was recorded at 552 nm [12]. The increased intensity of g3 SPR relative to that of g2 is attributed to the increased number of reduced Au NPs i.e. the Ag^+ ions play the role of catalyst in reduction of gold ions [4]. In addition, the loading of $AgNO_3$ markedly minimize the width of the SPR band which is considered as an indication of obtaining Au NPs with narrow particle size distribution.
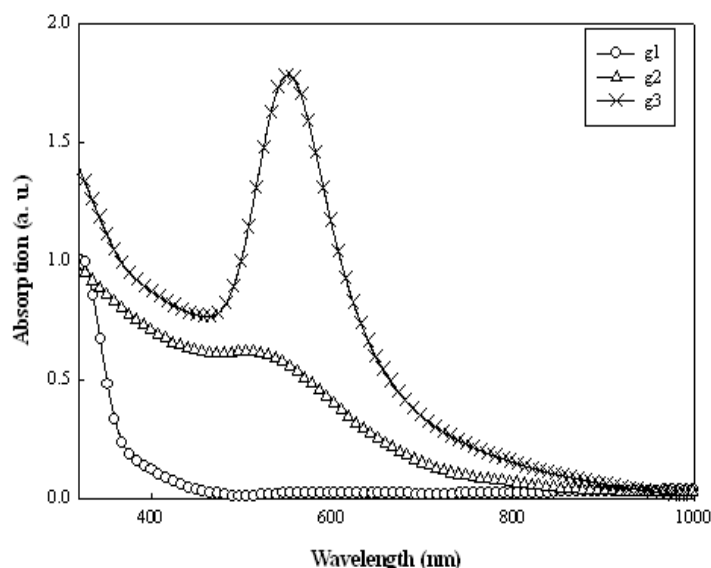
Figure 1 UV-visible absorption spectrum of the prepared samples.

Transmission electron microscope

The shape, size and size distribution of Au NPs obtained from sample g3 are displayed in Figure 2a, b. The gold nanoparticles are mostly spherical and pseudo-spherical-shaped particles. Although there is no stabilizing agent is used in the synthetic routs, the Au NPs are well separated from each other and no aggregates are observed. The average size of resulting particles is determined from the peak position of the Gaussian fitting which is about 23 nm. The narrow width of the Gaussian peak indicates a narrow size distribution of the prepared Au NPs obtained by this method.
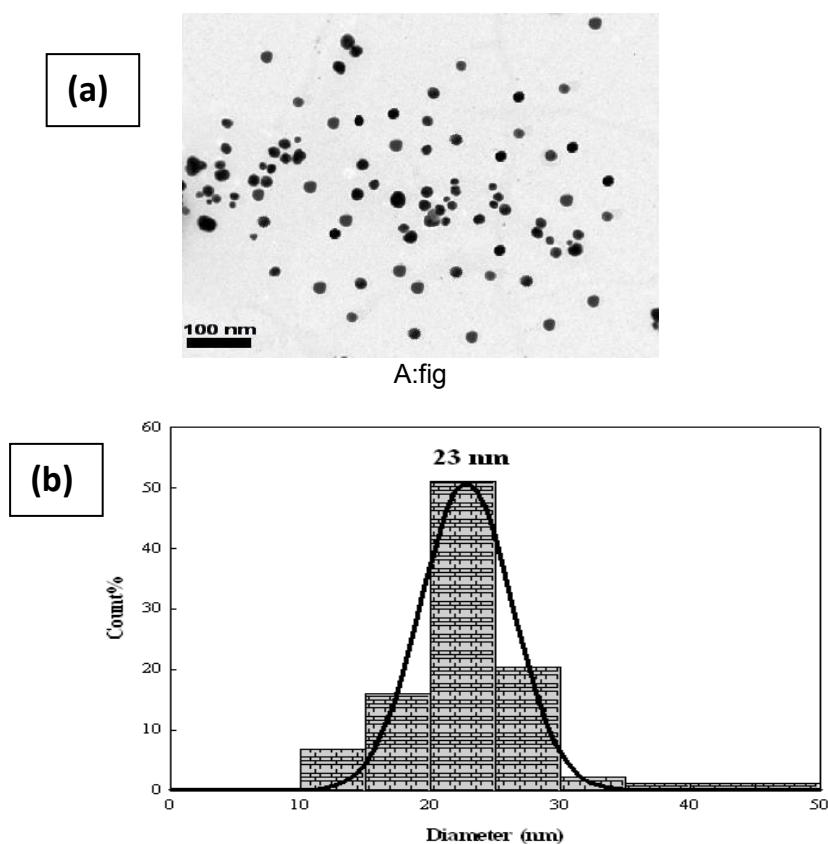
(a)

A:fig

(b)

Figure 2: (a) TEM image of Au nanoparticles and (b) the histogram of the particle size distribution with Gaussian fitting for the sample g3

X-ray diffraction studies (XRD)

Structural characterization has been performed using XRD analysis and the typical XRD pattern for PVA/Au nanocomposite is shown in **Figure 3**. The diffraction pattern is dominated with broad and shallow diffraction peak at around 2θ = 19.54°. This peak is attributed to the (110) reflection from a plane which contains the extended planar zig-zag chain direction of the crystallites [13-14].

In addition to the main diffraction peak of PVA (2θ = 19.54°), the diffraction pattern exhibit three new diffraction peaks. These are located at 2θ values of 38.2°, 44.6° and 64.46°. These prominent peaks are corresponding to (111), (200) and (220). The indexed diffraction lines revealed that the gold nanoparticles are formed in the PVA matrix and their crystal structure is cubic with face centered Bravias lattice [15]. This is a further confirmation of formation of Au NPs within PVA chains. It can be seen that the preferred growth plane of the particles is the (111) lattice plane which show the highest intensity all over the diffraction pattern.

The significant diffraction peak broadening and the corresponding low intensity of the signal were due to the small size of the nanoparticles. In particular, the peak broadening is inversely proportional to nanoparticle size. According to Scherrer's formula $D = k\lambda/\beta\cos\theta$ where k = 0.89 (shape factor in the case of spherical nanoparticles), λ = 1.54056 Å (X-ray wavelength for CuKα), β is line broadening at half the maximum intensity (FWHM) in radians and θ is the angle obtained from 2θ value corresponding to (200) peak in XRD pattern [16]. The average dimensions of Au nanoparticles prepared within PVA polymeric matrix is calculated and equal to 19 nm.
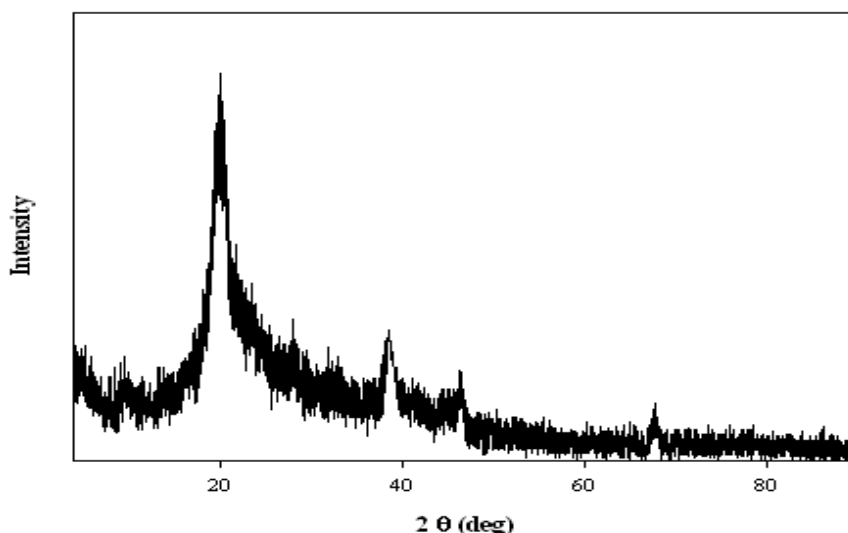

Figure 3: The X-ray diffraction patterns of 4 hr UV-irradiated PVA/Au nanocomposites loaded with 500 mL of AgNO₃.

Catalytic Degradation of Methylene Blue using PVA/Au Nanocomposite.

The as-prepared PVA/Au film was used in the aqueous reduction process of MB to investigate its possible applications in liquid-phase catalytic reactions

The aqueous solution of MB shows two distinct absorption peaks at 612 and 663 nm (see Figure 4a). No noticeable change on the intensity and position of these peaks upon addition of freshly prepared aqueous solution of NaBH₄. In the absence of proper catalyst, the intense blue color of MB solution remained unaltered for several days.

Figure 4(b, c) shows the behavior of catalytic degradation of MB in presence of PVA/Au nanocomposite film. The process was quantitatively monitored as a successive decrease in the both peaks height at 612 and 663 nm together. These spectroscopic data were corresponded to a change in solution color from blue to colorless during the time course of the reaction. The dramatic color fading confirms the success of our nanocomposite in catalytic degradation of MB.

Since the catalytic reduction reaction was carried in large excess concentration of NaBH$_4$ as compared with that of MB, the rate constant (K) could be assumed to be independent of NaBH$_4$ concentration. Hence, the catalytic reduction reaction is considered as pseudo-first-order kinetics with respect to MB concentration. The rate constant (K) of the catalytic reaction can be estimated by the following relation [17];

$$\frac{dC_t}{dt} = KC_t \ \ or \ \ \ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = \text{-Kt}$$

Where C_0 and C_t are the concentration of 4-NP at the beginning and time t of the reaction while A_0 and A_t are their corresponding absorptions, respectively.

Figure 4d shows the graphical plots of ln (A_t/A_0) *vs* the reaction time (t). The plots presented a good linear relationship between ln (A_t/A_0) and the reaction time (t). The slopes of these relations determines the rate constant (K) of the reaction. Figure 16 represented a good linear relation of ln(*A*) versus time. The estimated reaction rate constant was estimated to be (1.35 ×10^{-3} and 1.29 ×10^{-3}) sec^{-1} for the 1st and 2nd run respectively.

The atomic absorption spectrometry was used to determine the traces of Au NPs that segregated from the polymer network during the catalytic degradation experiment after each run. The obtained results showed that no Au NPs were leached from the PVA matrix confirming the success of Au NPs immobilization within PVA chains. This is considered of technical importance where the gold nanoparticles can be easily recovered from the reaction medium and easily used again.
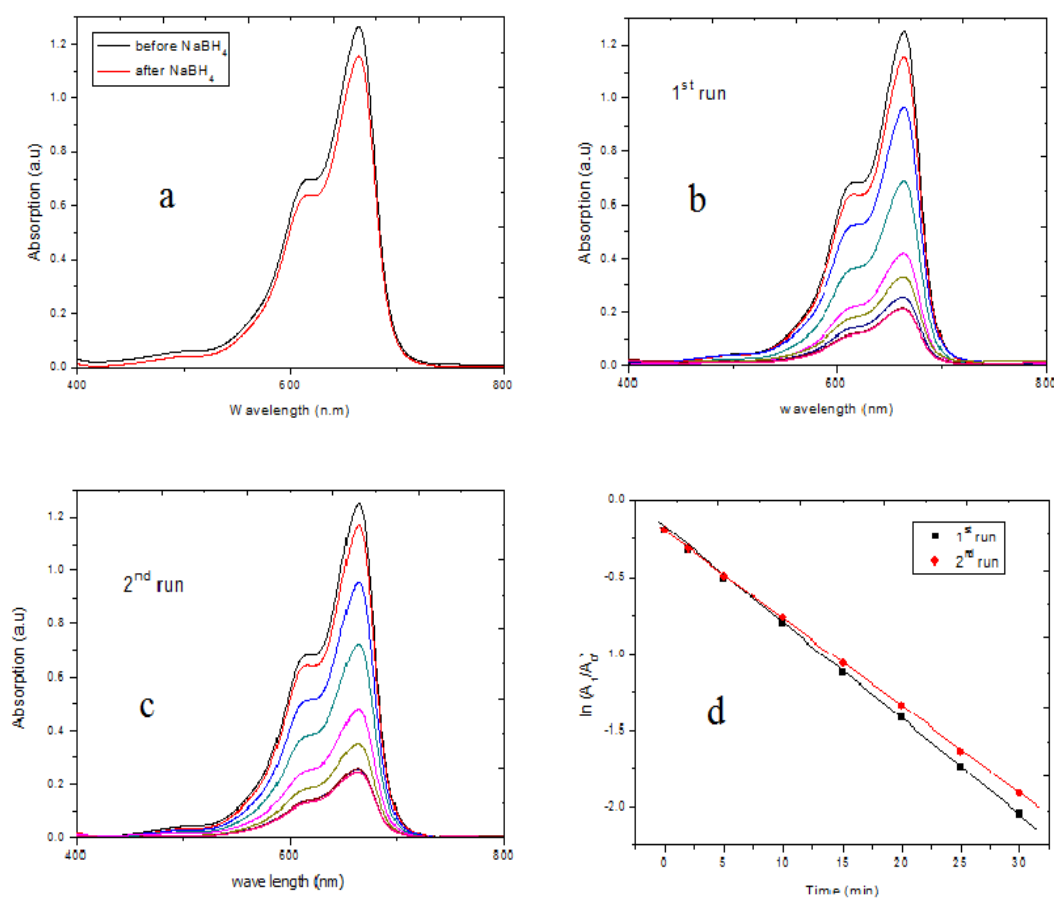

Figure 4: (a) UV-vis absorption spectra of MB before and after addition of NaBH$_4$. (b)Time-dependent UV-vis absorption spectra for catalytic degradation of methylene blue by PVA/Au nanocomposites for first and (c) for second run. (d) ln(A$_t$/A$_0$) versus reaction time.

Impact of initial MB concentration

The effect of the initial MB concentration on the catalytic degradation reaction depends on the immediate relation between the dye concentration and the available binding sites on a catalytic surface [18]. Fig.5 shows the effect of initial dye concentration (0.339×10^{-5}M, and 1.578×10^{-5} M) on the rate of catalytic degradation reaction. The calculated rate constant for low and high concentrations are (0.59×10^{-3} and 1.35×10^{-3}) sec^{-1} respectively. Generally the percentage of dye degradation increases with an increase in initial dye concentration [19]. This may be due to the high driving force for mass at a high initial dye concentration [20].
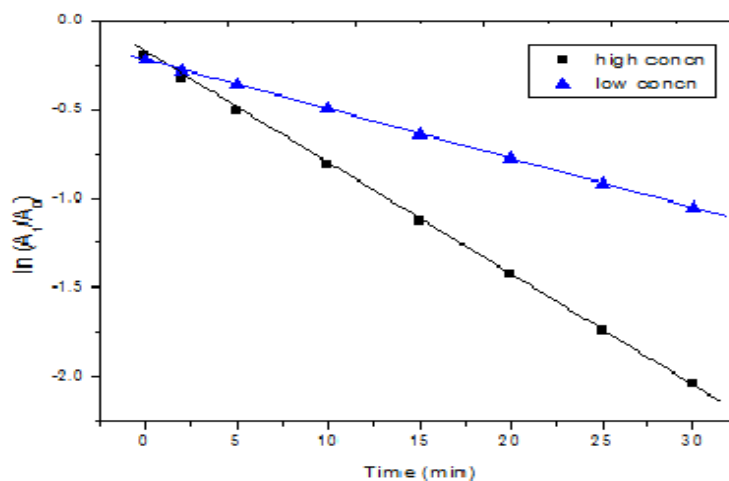

Figure 5: $\ln(A_t/A_0)$ versus reaction time for catalytic degradation of MB at different concentration

CONCLUSION

Gold nanoparticles with monodispersed size and spherical shape were grown successfully within PVA matrix under UV irradiation. The PVA/Au nanocomposite film is confirmed to be an efficient catalyst during degradation process of MB by using $NaBH_4$. The PVA/Au catalyst can offer several advantages, such as 1) The ease of preparation without need for complicated experimental setup, 2) Using the very cheap PVA as a supporting matrix for the Au nanoparticles to anchor, which significantly reduce the aggregation of Au nanoparticles, 3) The PVA/Au catalyst can be easily handled and removed from the reaction medium i.e. there is no need for filtration and/or separation processes which result in expensive and complex processes, 4) It can be rapidly gathered for recycling

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