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Facile Synthesis, Characterization and Catalytic Function of Gelatin Stabilized Gold Nanoparticles

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Abstract

In the present investigation, we report a new one phase, one pot method for synthesis of 3.5 ± 0.7 nm average sized gelatin capped gold nano particles (Gel-AuNPs) using strong reductant $NaBH_4$ in aqueous system at room temperature. Size controlled Gel-AuNPs were characterized by UV-Visible, STEM, XRD, DLS and FT-IR. Spherical Gel-AuNPs showed excellent catalytic activity for reduction of three differently charged dyes eosin B (EB), methylene blue (MB) and rose bengal (RB) in the presence of $NaBH_4$. The study revealed that 100% reduction of EB, MB and RB dyes was carried out in just 150 sec. The developed catalyst was easy to recover and capable to be reused three times. The process of reduction rate and kinetics of dyes was monitored using UV-Visible spectrophotometer. A plot of lnC Vs time (sec) showed that reaction follows the first order kinetics. Rate constant (K) was determined for EB, MB and RB reduction at 10 μM, which was found as 2.735×10^{-2} sec^{-1}, 2.738×10^{-2} sec^{-1} and 2.55×10^{-2} sec^{-1}, respectively. The study revealed that catalytic reduction of dyes by Gel-AuNPs in aqueous medium is environmental friendly in terms of recovery of catalyst, is exceptionally fast and hence extremely economical.

Keywords: Gelatin; Controlled; Catalytic activity; Dyes; Recovery.

Introduction

Nanotechnology has brought diverse disciplines together and this interdisciplinary approach is anticipated to contribute innovations that might solve many of today's challenges in society. Noble metal nano particles (MNPs) display unique, superior and indispensable properties such as size dependent chemical, electronic and optical properties, their uniqueness arises specifically from their size, shape, higher surface to volume ratio and increased percentage of atoms that are unavailable in conventional macroscopic materials. Nevertheless, AuNPs have potential applications in different fields such as electronics, health, medicine, transportation, energy and environment [1]. There is continuous research towards synthesis of MNPs using inexpensive and nontoxic chemicals, environmentally benign solvents, clean and renewable/ biodegradable materials [2, 3]. Considering green nature of these approaches, reducing agents, capping agents and reaction medium are three key factors in synthesis and stabilization of MNPs. AuNPs in the solution are very active and prone to coagulate due to vander waals forces and high surface energy unless they are protected. In this regard numerous capping agents and surfactants have been used to protect AuNPs from aggregation. They include cetyltrimethylammonium bromide (CTAB) [4], tetrahydrothiophene (THT) [5], 1-Phenyle- 5-thiotetrazoles [6], 11-mercaptoundecanoic acid [7], benzene and anthracene [8], ciprofloxacin [9], resorcinarene [10], polyethylene glycol [11], didodecyldimethylammonium bromide [12], aromatic thiols [13] etc. Most of these capping

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agents are health hazardous organic compounds. These capping agents can be replaced by environmental friendly natural polymers such as gelatin, proteins, chitosan and starch. These are biodegradable and bio absorbable with degradation products that are non-hazardous. Gelatin is hydrolytically and thermally denatured product of collagen, the most abundant protein found in animals and has been used extensively in food, industrial, pharmaceutical and cosmetic products, as binder material and photographical applications owing to its unique functional and technological properties that's why it is produced on a large scale at relatively low cost [14, 15]. At high temperature gelatin remains in the form of flexible, unfolded coils in the solution and can be partially re-natured to ordered, collagen-like helixes upon cooling at room temperature [16, 17]. Mostly natural collagen proteins obtained from animals are insoluble in water but gelatin is freely soluble in polar solvents such as water at ~35 ^{0}C, due to hydrogen bonding [18]. Several synthetic methods using unfolded gelatin capped Au and AgNPs have been developed at high temperature (100 ^{0}C**)** [19, 20, 21]. However it is reported that above 55 ^{0}C gelatin becomes denatured and looses its origin; surprisingly very little attention has been paid towards gelatin usage at low temperature. So, still there is a need to use gelatin at room temperature as capping agent. Gold is considered as inactive metal for catalysis because of its inertness [22]**,** but when it is brought into small particle less than 10 nm, it turns out to be surprisingly active for many reactions, such as CO oxidation and propylene epoxidation at low temperatures [23]. Haruta et al. deposited very small 3-10 nm sized AuNPs on metal oxides, such as TiO_2, Fe_2O_3, Co_3O_4 and NiO, which displayed surprisingly high catalytic activity for CO oxidation at low temperature (-70 ^{0}C) [24]. Mitsudome et al have synthesized Hydrotalcite-AuNPs and used them as highly efficient, selective and reusable catalyst for an aerobic oxidation of 1-phenylethanol into acetophenone [25].

Today dyes are among the most common organic industrial pollutants, such as textile, plastics, paper, food, leather, cosmetics etc. are major source of producing toxic species in the form of colored waste waters. These colored species are producing great disturbance in photosynthetic process in aquatic plants due to meager light penetration [26 – 30]. According to another report some of azo-dyes and their degradation products such as aromatic amines are highly carcinogenic [31]. Many processes have been developed for decolorization of dyes, achieved through adsorption [32], degradation [33 – 35], oxidation [36, 37] and catalytic reduction [38–41]. However, due to the reasons of energy saving, safe operation and avoiding use of organic solvents, it may be interesting and meaningful to develop process for detoxification in aqueous solution under mild condition. Also, the process could be used for treatment of wastewater which contains mainly dyes without complicated composition.

The aim of our study was to synthesize small Gel-AuNPs and investigate activity as heterogeneous, recoverable and reusable catalyst for exceptionally faster and complete reduction of EB, MB and RB dyes. To the best of our knowledge there is no easy and quick method by which Gel-AuNPs are reported for catalysis of dyes at room temperature. Therefore here we report easy quick and one step method for synthesis of well stabilized Gel-AuNPs and their catalytic activity.

Experimental Section

Chemicals and Reagents

Analytical grade $HAuCl_4.3H_2O$, $NaBH_4$, NaOH and gelatin were purchased from Sigma-Aldrich (St. Louis, MO) HCl, methylene blue (MB), rose bengal (RB), eosin B (EB) dyes purchased from (Fluka) and used without further purification. All acidic, basic and salt solutions were prepared in milli Q water.

Instrumentation

Gel-AuNPs were characterized by UV-Visible spectrophotometer model lambda 2 of Perkin Elmer(USA). FT-IR spectra were recorded by Niclolet Avtar 5700 FT-IR spectrophotometer of thermo (USA), STEM observations were carried out using a TECNAI electrom microscope (FEI company (USA) operated at an accelerating voltage of 300 kV; zeta potential was performed by Malvern Instruments Corporation (UK) and XRD was carried out using RIGAKU RTAFLEX RAD-B of Rigaku corporation (Japan) with CU-K α radiation with wavelength of 1.315 Ã, 40 kV, 100 mA, to scanning rate 0.005°/sec and step size 0.02 specifications.

Synthesis of Gel –AuNPs

To a 0.13 mL (0.15%) $HAuCl_4.3H_2O$ solution of pH 4, was added sufficient amount of milli Q water followed by 0.1 mL of (0.1M) NaOH and 0.05 mL of freshly prepared 0.1M $NaBH_4$ and 0.5 mL (0.5%) gelatin. The final volume was adjusted to 10 mL; this mixture was stirred vigorously with glass rod for approximately (1-2 min) until solution turned into transparent light pink color. Gelatin solution (0.5%) was prepared in milli Q water; 0.5% gelatin solution was prepared at 45 ^{0}C.

Preparation of Gel-AuNPs sample for STEM

Gel-AuNPs sample for STEM was prepared by placing 5 µL drops on carbon coated copper grid and dried at room temperature.

Preparation of Gel-AuNPs samples for XRD

According to method, a bulk solution (100 mL) with above mentioned concentration of each reagent containing synthesized Gel-AuNPs were fabricated and transferred into centrifuge cells. The process of centrifugation was carried out for 1 h at 6000 rpm. Upper portion of Gel-AuNPs was drained carefully and lower portion of approximately 1 mL was collected. With the help of micro pipette, the drop from collected portion of Gel-AuNPs was placed on glass slide, which was already put on hot plate at 100 ^{0}C.

Sample Preparation for FTIR Spectroscopy

Bulk solutions (2000 mL) containing appropriate amount of $HAuCl_4.3H_2O$ solution, H_2O, NaOH, $NaBH_4$ and gelatin were mixed in similar way as mentioned above for Gel-AuNPs synthetic. Synthesized Gel-AuNPs were transferred into big petri dishes, dried at 100 ^{0}C followed by N_2 treatment for 5 minutes and washed 2-3 times with methanol and water to remove any un-reacted materials. The dried sample was scratched off with clean glass slide and collected in sample holder before study.

Preparation of Gel-AuNPs as Heterogeneous Catalyst

Gel-AuNPs were accommodated on small pieces of glass cover slips and dried under N_2 for ten min. These glass pieces were weighed before and after treatment of Gel-AuNPs to find out the amount of Gel-AuNPs by difference. Gel-AuNPs in the range of 0.03 to 0.15 mg were used in catalysis experiments.

Catalytic reduction of dyes

The catalytic reduction of EB, MB and RB dyes were carried out in a standard quartz cell with 1 cm path length and about 4 mL volume containing Gel-AuNPs loaded pieces of glass. This reaction was performed in the presence of little quantity of $NaBH_4$ alone and Gel-AuNPs. Under optimized conditions, the catalytic reaction procedure was as follows for each individual dye i.e. 0.4 mL of each individual dye was taken from 100 µM standard solution, to which was added 2.80 mL of milli Q water followed by 0.8 mL of 0.1M $NaBH_4$. Carefully and immediately after addition of 0.12 mg, Gel-AuNPs were immobilized on pieces of glass and put in quartz cell for reduction process. The absorption spectra were monitored by a UV/Vis spectrophotometer with a time interval of 50 sec in a scanning range of 450–750 nm at room temperature.

Results and Discussion

In order to produce very small Gel-AuNPs, various optimization studies were carried out such as pH (2-9 levels), concentration of $HAuCl_4$, $NaBH_4$, NaOH and gelatin. By doing so we observed that maintaining pH 4 of 0.13 mL $HAuCl_4$ in aqueous solution in which was added 0.1 mL of (0.1M) NaOH followed by 0.05 mL (0.1M) of $NaBH_4$ and 0.5 mL (0.5%) gelatin produced best λ_{max} of 520 nm, indicating characteristics for formation of Gel-AuNPs [42] as shown in Fig. 1(a). Final pH of synthesized Gel-AuNPs was measured and found as 9.4. Effect of gelatin concentration on absorption band of AuNPs is shown in Fig. 1(b). A 7 nm blue shift was observed in SPR band by increasing gelatin concentration from 100 µL to 600 µL using 0.5% gelatin solution. Gelatin monomers contain amino functional group which possesses high affinity towards noble metals; they are often used to anchor MNPs on to different substrates and short wavelength was observed in the Gel-AuNPs [20]. Stability of Gel-AuNPs was tested and results show that particles are stable up to eight days.

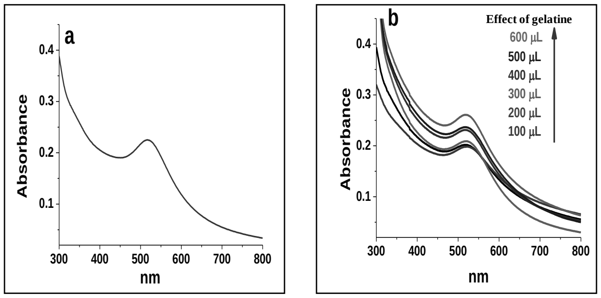

Figure1. **(a) Showing Surface plasmon resonance band of Gel-AuNPs (b) Effect of different concentration 0.5% gelatin.**

Scanning Transmission Electron Microscope (STEM) can provide valuable and accurate information about size, shape and monodispersity of Gel-AuNPs [43]. In our experiments, STEM was used to investigate well dispersed morphology of Gel-AuNPs and their capping with gelatin network as shown in Fig. 2(a-d). Typical STEM images and a corresponding histogram for Gel-AuNPs are given in Fig. (2d). Size of Gel-AuNPs was calculated as 3.5 ± 0.7 nm. Narrow size distribution is obvious in STEM micrographs; however, further analysis reveals that separation among Gel-AuNPs is very remarkable. Spherical Gel-AuNPs are fairly dispersed and well separated in gelatin; because it has free amine group, which leads to protonation in acidic medium. Positive charge on amine group strongly interacts with AuNPs, maintaining triple helix tail chain which forms provides steric hindrance around NPs. STEM results exactly coincides with corresponding SPR band of UV-visible; therefore gelatin surface can protect AuNPs from coagulation and acts as better stabilizer than conventional surfactants. The interaction of AuNPs with gelatin was characterized by FT-IR. FTIR of pure gelatin and Gel-AuNPs are shown (Fig. 3) in which we have observed disappearance and shifting of some peaks. The main clue from which we can get about interaction of AuNPs with gelatin, neutralization of –NH$_3^+$ and in gelatin strong adsorption at 1556 cm^{-1} shows presence of –NH$_3^+$ group [45], while in Gel-AuNPs –NH the peak is disappeared. It means that positively charged –NH$_3^+$ interacted with negatively charged AuNPs. Neutrality of Gel-AuNPs also matches to results of zeta potential. In gelatin the peak at 1455 cm^{-1} confirms carbonate CO$^-_3$ ion, however this vibrational band is shifted at 1386 cm^{-1} in Gel-AuNPs. It shows the presence of sodium salt, while bands at 1069 cm^{-1} and 1006 cm^{-1} confirm C-C in gelatin as well as Gel-AuNPs.

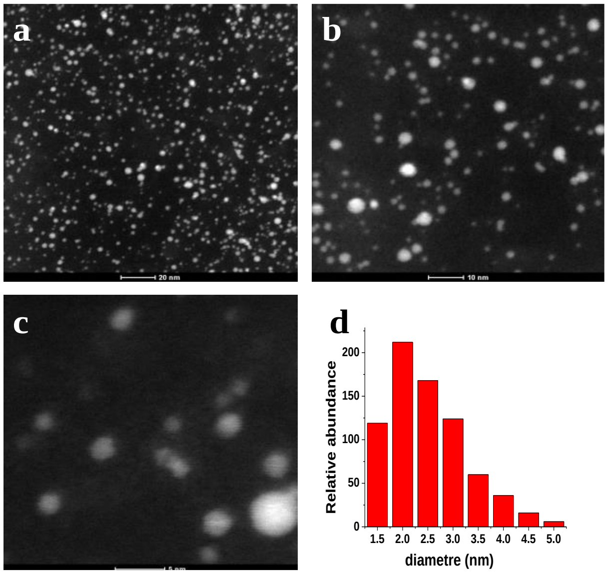

Figure 2. **(a-b) STEM micrograph showing gel-AuNPs at different magnifications and corresponding size distribution histogram of Gel-AuNPs (Fig. 2a).**

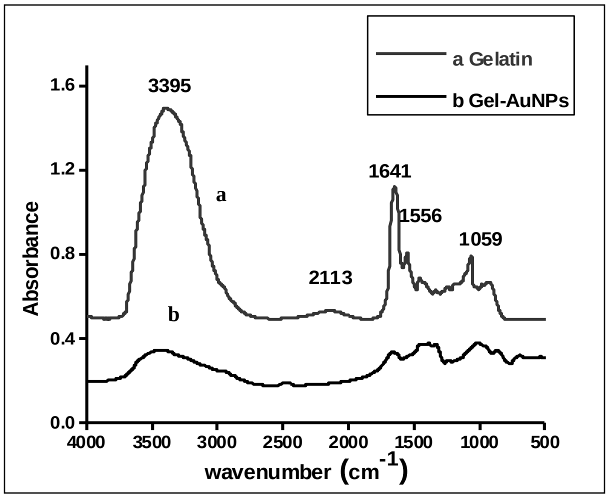

Figure 3. **FTIR showing (a) pure gelatin (b) gelatin capped gold nanoparticles.**

In order to determine formation of crystal phase and atomic arrangement of Gel-AuNPs, XRD analysis was performed. XRD patterns of Gel-AuNPs were achieved at 2θ scale, 38.2^0,

44.4^0, 64.8^0 and 77.7^0 that correspond to (111), (200), (220) and (311) plans of standard cubic phase of Au crystals [44] as shown (Fig. 4). These all peaks clearly indicate the presence of face centered cubic and body centered cubic patterns in Gel-AuNPs sample. Moreover broadening of XRD peaks confirms small size of Au. The average size, 3.2 ± 0.5 of Gel-AuNPs was also confirmed from width of diffraction peak using Debye-Scherrer equation. This equation can be described as d = Kë/B cos θ, Where d stand for particle size, *K* represents Scherrer constant; its value is (0.89), ë indicates X-Ray wavelength (Cu Ka, 1.54056 A°), θ represents the diffraction angle and *B* is the corrected full width at half maximum (in radian).

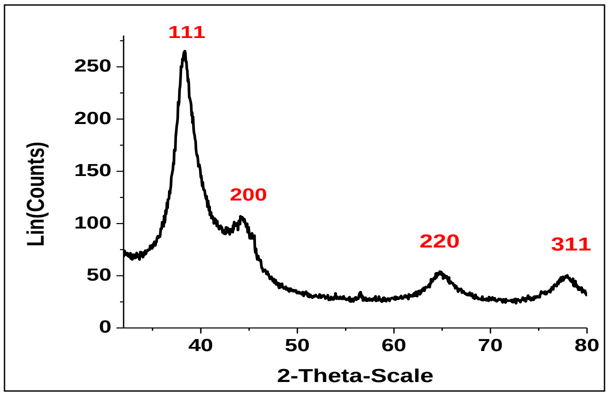

Figure 4. **X-Ray diffraction (XRD) pattern showing Gel-AuNPs.**

The Zeta potential of Gel-AuNPs was performed using Malvern Instruments Corporation and it is electrostatic potential present at shear plane of MNPs, which is associated with both surface charge and local environment of NPs. For Gel-AuNPs, the Zeta potential was measured as 0.0 ± 0.8 mV which is neutral as shown (Fig. 5).

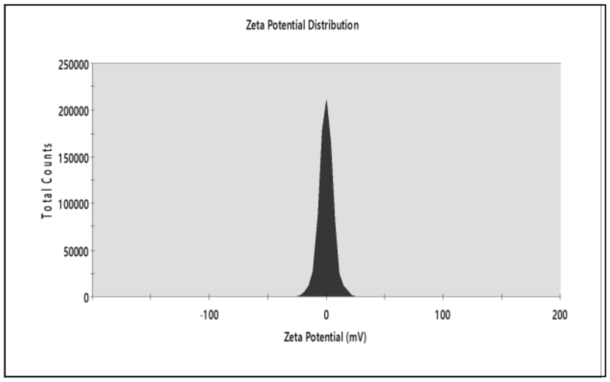

Figure 5. **Zeta potential spectrum of gelatin capped gold nano particles.**

Catalytic reduction of dyes

To investigate catalytic efficacy of Gel-AuNPs in aqueous system, three differently charged dyes such as EB, MB and RB were selected. During working conditions, MB becomes cationic, EB is anionic and RB is neutral. SPR band of EB, MB and RB appeared at 515 nm, 663 nm and 547 nm respectively in aqueous solution. Reduction of each individual dye was observed with $NaBH_4$ in absence of Gel-AuNPs; for half an hour, it was noticed that in the absence of catalyst, strong reducing agent $NaBH_4$ is unable to reduce EB, MB and RB. It reduces EB, MB and RB up to small extent, 8.1%, 8.7% and 10% respectively as shown (Fig. 6 (a-c)). In agreement with previous results [46, 47], the reduction of dyes by $NaBH_4$ did not occur to an appreciable extent in the absence of Gel-AuNPs; however, the catalytic efficiency of Gel-AuNPs can be confirmed from Fig. 7 (a-c) which shows a large decay in concentration of EB, MB and RB in the presence of Gel-AuNPs. The entire reduction process is completed in just 150 sec at 25 °C. Interestingly, on addition of little amount of glass supported Gel-AuNPs (0.12 mg) to reaction system caused a fading and ultimate bleaching of EB, MB and RB dyes in aqueous solution. This suggests reduction of three different charged dyes by Gel-AuNPs in the presence of $NaBH_4$ within 150 sec. To exclude possibility that reduction reaction might be activated by Gel-AuNPs, sufficient quantity of Gel-AuNPs (0.12 mg) alone was added into aqueous solution of dyes but no change was observed in the concentration of EB, MB and RB even after 30 min. This indicates that Gel-AuNPs play role of a catalyst for reduction of dyes in the presence of reducing agent. Moreover, succession of catalytic reduction of dyes can be easily monitored by change in SPR band at wavelength of the absorbance maximum (max) of dyes. (Fig. 7 (a-c)) shows evolution of UV-visible spectra of dyes during their catalytic reductions when mixture of each individual dye, the Gel-AuNPs supported on glass and $NaBH_4$ are involved in reaction. Evidently, the absorbance of dyes gradually decreases with reaction time, which is indication of reduction of dyes. As expected, the catalytic reduction of dyes proceeds successfully and no deactivation or poisoning of catalyst was observed. Moreover, several optimization studies pertaining to the amount of Gel-AuNPs and NaBH$_4$ were carried out to improve rate of reduction of dyes in which we observed that rate of reduction of dyes rapidly increased with increase in concentration of Gel-AuNPs and NaBH$_4$. The reaction was observed at once, upon addition of Gel-AuNPs into quartz cell and each spectrum was recorded after interval of 50 sec, ultimately entire reduction process at 10 µM of dyes completes within 150 sec. It was noticed that reduction of dyes are almost linearly dependent upon quantity of Gel-AuNPs; 100% reduction of dyes was completed in just 150 sec. In this context, first-order kinetics could be used to evaluate kinetic reaction and rate of current catalytic reaction as shown (Fig. 8 (a-c)). Plot of lnC Vs time (sec) shows that reaction is undergoing through first order kinetics; rate constant (K) was determined for EB, MB and RB reduction at 10 µM as 2.735 x10^{-2} sec^{-1}, 2.738 x 10^{-2} sec^{-1} and 2.55x10^{-2} sec^{-1} respectively.

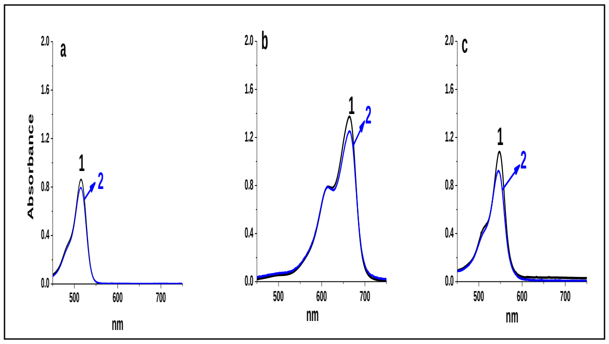

Figure 6. **(a) 10 µM Surface plasmon resonance band of (a1) Eosine B (b1) Methylene blue (c1) Rose bengal Fig:6(a2) 10 µM (A) Eosine B (b2) Methylene blue (c2) Rose bengal in the presence of 400 µL 0.1M NaBH$_4$ after half an hour.**

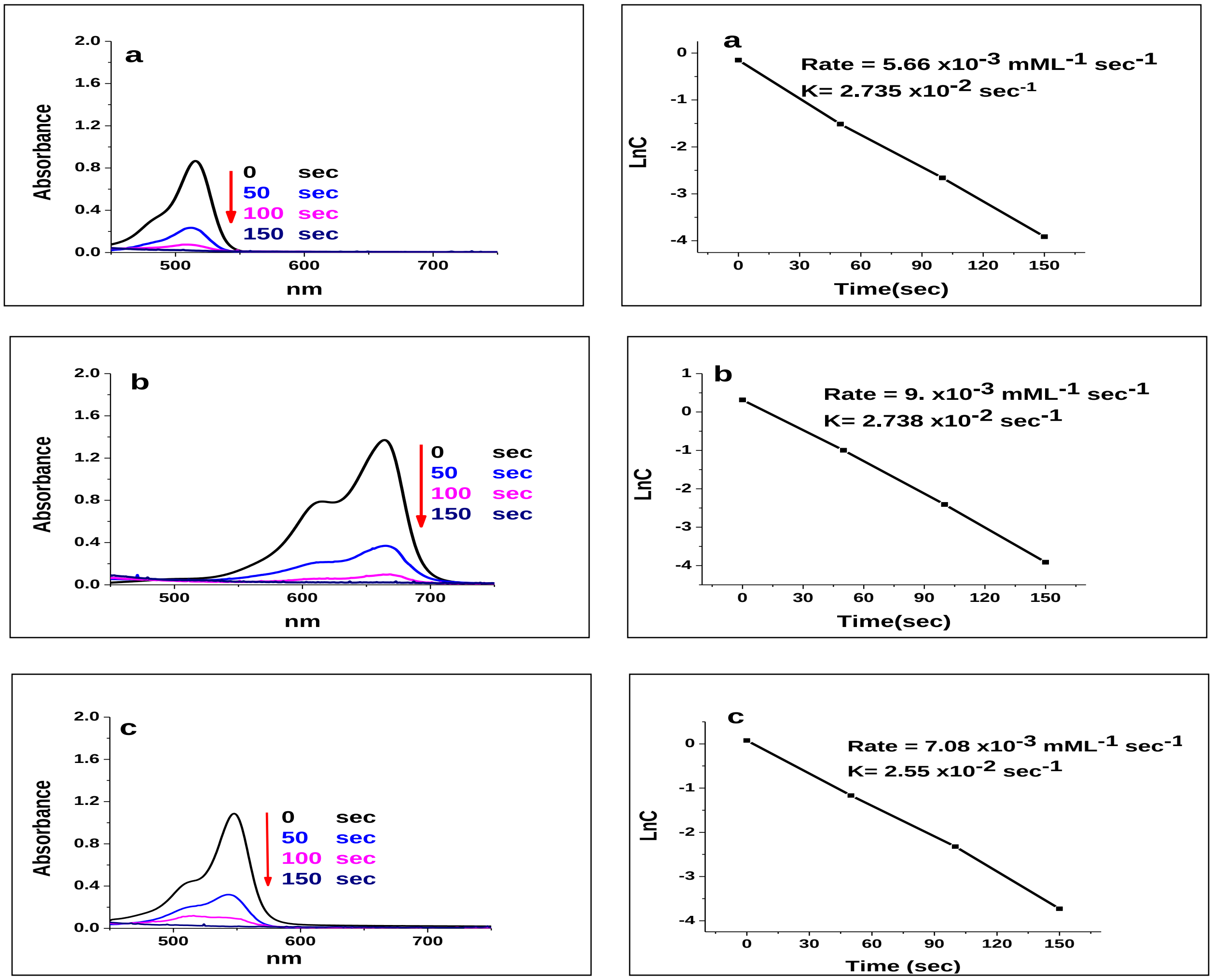

Figure 7. **(a) Plot of lnC Vs Time (sec) showing first order kinetics at 10 µM of each dye (a) EB (b) MB (c) RB reduction using Gel-AuNPs as catalyst.**

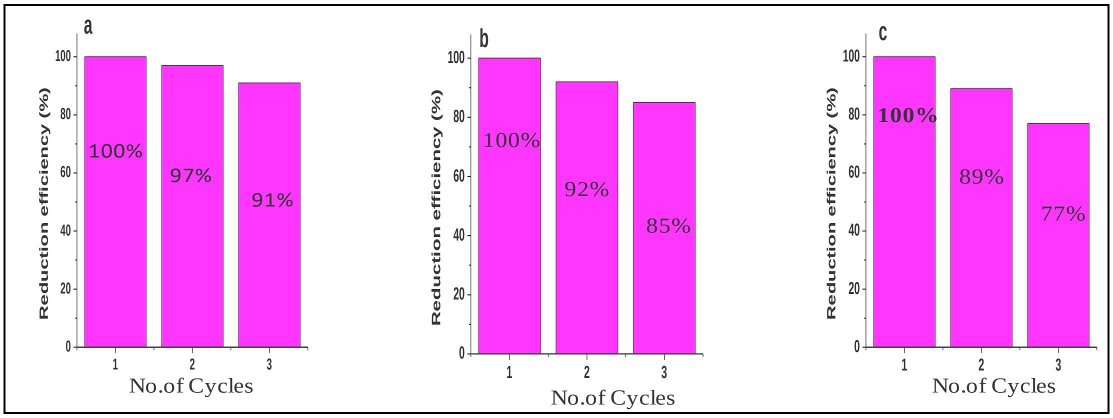

Figure 8. **Percent reduction potential of glass supported Ge-AuNps recovered and re-used for 3 successive cycles (a) EB(b) MB (c) RB.**

Recycling of Gel-AuNPs as Catalyst

Glass supported Gel-AuNPs (0.12mg) were removed washed susccessively and reused 3 times for catalytic reduction of three differently charged dyes at10 µM. The reducing potential of recovered and reused Gel-AuNPs for each dye was calculated, which is given (Fig. 8). It is apparent that potential of Gel-AuNPs for catalytic fading of color decreases; however the decrease in activity is still not very low. This behavior confirms that recovered Gel-AuNPs are highly active despite some possible loss during each repeated washing. The slow deactivation of catalysts (Gel-AuNPs) also confirms that poisoning of catalysts is negligible.

Conclusion

Easier, rapid and one pot synthesis with mean size 3.5 ± 0.7 nm Gel-AuNPs was performed at room temperature. Fabricated Gel-AuNPs were characterized successfully by UV-visible, STEM, XRD, DLS and FT-IR. Synthesized Gel-AuNPs proved as exceptionally efficient catalyst for reduction of EB, MB and RB dyes. The work offers cheap solution to aquatic environment in terms of time saving, use of little amount of catalytic Gel-AuNPs and is equally useful for reduction of several other organic compounds.

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