

Urchin-like cobalt nanostructures for catalytic degradation of nitro anilines

Abdul Rauf Khaskheli^{1,5*}, Saba Naz^{2,5}, Faruk Özel³, Abdalaziz Aljabour³, Sarfaraz Ahmed Mahesar⁴, Imren Hatay Patir⁵, Mustafa Ersoz^{3,5}

¹Department of Pharmacy, Shaheed Mohtarma Benazir Bhutto Medical University Larkana 77170, Sindh, Pakistan

²Dr. M. A. Kazi Institute of Chemistry, University of Sindh Jamshoro 76080, Pakistan

³Karamanoğlu Mehmetbey University, Metallurgical and Materials Engineering Department, 70200 Karaman, Turkey

⁴National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

⁵Department of Chemistry, Faculty of Science, Selcuk University, Konya 42075, Turkey

*Corresponding author. Tel: (+92) 3332617777; Fax: (+92) 8749410910; E-mail: arkhaskheli@gmail.com, farukozell@gmail.com

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ABSTRACT

The undertaken study describes synthesis of urchin-like Cobalt nanostructures (Co NSs) in aqueous solution using gallic acid as both reductant and protecting agent for the catalytic degradation of 4-methyle-2-nitroaniline. UV-Visible (UV-Vis) spectroscopy was used as a primary tool to elaborately study and optimizes the necessary experimental condition for the developed synthetic protocol Fourier transform infrared (FTIR) spectroscopy showed the interaction between gallic acid and the surface of Co NSs via -OH linkages although Scanning electron microscopy (SEM) confirmed the formation of urchin shaped nanostructures with diameter in the range of 80-110 nm and length of tentacles between 1.0 – 1.8 μm . The as-synthesized Co NSs proved to be excellent heterogeneous catalyst for the 100 % reductive degradation of 4-methyle-2-nitroaniline in just 60 sec in presence of reductant (NaBH_4) with reaction rate calculated to follow pseudo first order kinetic and rate constant of 0.055s^{-1} . Furthermore, Co NSs, showed excellent recyclability and were reused four times for the degradation of 4-methyle-2-nitroaniline with efficiency that displayed negligible catalytic poisoning. Copyright © 2016 VBRI Press.

Keywords: Co nanostructures; urchin morphology; 4-methyle-2-nitroaniline; catalyst.

Introduction

Research in nanomaterial's has achieved significant attention because of their unique properties and numerous applications in different areas [1]. The capability to fashion metal nanostructures with variety of shape and sizes allows exploring their fascination applications in fields like catalysts, absorbents, chemical and biological sensors, optoelectronics, information storage, photonic, electronic devices and so on [2]. Several study reported behavior of nanomaterials influenced by their shape like anisotropic optical behavior for zinc oxide and nickel nanowires during hydrogenation of alcohols [3, 4, 5]. Thus, as a consequence of such unique behaviors compared to their common obtained morphologies, special shaped nano-composite materials are the focus of present day scientific research. Literature reported the several methods for the synthesis of nanostructures include solvothermal process [6], thermal decomposition method [7], hydrothermal micro emulsion process [8], high temperature solution phase method [9], and wet-chemical reduction method [10].

In the above-mentioned methods, the chemical reduction method has the benefit over the others in easy control of the reaction process and production rate. However, most of wet chemical reduction methods reported to date rely heavily on organic solvents and use environmentally and biologically hazardous reducing agents *i.e.* Hydrazine,

sodium borohydride, dimethyl formamide, potassium bitartrate, formaldehyde, sodium hypophosphite or hydroxylamine hydrochloride, etc. [2, 9]. Owing to their toxic nature considerable attention has been given the usage of green environmental friendly and economic materials for practical field applications. Sharma *et al.* demonstrated the green fabrication of gold nanoparticle with tea leave in aqueous media [11], Vigneshwaran *et al.* worked on the one pot green synthesis of silver nanoparticle via soluble starch [12] Xiong, *et al.* recently reported synthesis of highly stable dispersions of nanosized copper particles with an average particle size less than 2 nm using a nontoxic L-ascorbic acid as both a reducing agent and capping agent precursor in aqueous medium [13] another effort towards green synthesis of anticancer Palladium nanoparticles reported by Gurunathan *et al.*, using leaf extracts of *Evolvulus alsinoides* [14].

The use of nano size metal structures as a heterogeneous recyclable catalyst in various environmental problems associated with hazardous wastes and toxic water pollutants pollution is the need of the day [15]. For instance, nitro aromatic compounds are commonly employed as a precursor for the synthesis of pharmaceuticals, azo-dyes, gum inhibitors, poultry medicines, and as a corrosion inhibitor. While these compounds caused toxicity if release into the environment [16-18]. As a result of toxicity, public

concern has prompted the need to develop clean-up greener technologies for restoration of environments. Junejo *et al.* reported the enhanced catalytic degradation of nitro anilines using ceftriaxone drug capped silver (Ag) nanoparticles [19-20].

About all the previous reports focused on the usage of precious metals like silver, and gold in the field of catalysis. However, such metals due to their high cost, and troublesome availability restricts their applications in larger volume production. In such perspective cobalt can serve as a suitable alternative with its low cost, easy availability and its catalytic properties closely matching with those of platinum [21-22]. Thus it can serve as a model catalyst for cheap metal nanostructures based environmental remediation processes. In addition, Cobalt also possesses higher electronic and thermal conductivity, compared to traditional noble metals like silver gold and platinum [23]. In spite of the various aforementioned efforts towards formation of stable nanostructures, the usage of green strategy for cheap and efficient nanostructures is still a challenging task.

Therefore, the undertaken study was aimed to develop a sensitive, robust, cost effective and environmental friendly method for one-step fabrication of biocompatible highly stable urchin-like cobalt nanostructures by using gallic acid as reductant and stabilizing agent. As mentioned before that the properties of nonmaterial are highly dependent on their shape so a catalytic reductive degradation experiment of model nitro compound particularly 4-methyl-2-nitroaniline was also brought under study to explore the catalytic and kinetic behaviors of cobalt nanostructures which to the best of our knowledge, have not been reported for urchin-like cobalt NSs before.

Experimental

Materials and reagents

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99.9 %), gallic acid (99 %), HCl (37 %), and sodium hydroxide (99 %) were obtained from Sigma-Aldrich, ACS reagent. 4-Methyl-2-Nitroaniline were purchased from E. Merck. All the obtained chemicals were used as received without further purification employing pure Milli-Q water as the preparatory medium.

Procedure for fabrication of urchin-like Co NSs

In a typical synthesis 25 mL of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5mM) was taken in a 50 mL conical flask. The solution was stirred at room temperature followed by addition of 4.5 mL gallic acid (2.5mM). The solution was stirred for few minutes and then pH was adjusted to 10.0 with addition of 0.1 M NaOH. The change in color of solution was observed to change from light pink to brown indicating reduction of cobalt ions. The solution was allowed to stir for 10 min to achieve complete reduction reaction. The as synthesized Co NSs were then separated from solution by high speed centrifuge, washed with deionized water and ethanol to remove unreacted Gallic acid and impurities respectively.

Characterization

UV-visible spectroscopy (Lambda 35 of PerkinElmer) was used for optical confirmation of Co nanostructure in the

spectral range of 200-800 nm. Fourier transform infrared spectroscopy (FTIR) Vertex 70 Bruker, (Germany) was used for studying surface interaction of Co nanostructures with gallic acid. Morphological characterization with size determination was performed using Scanning electron microscopy (SEM) EVO LS 10, AEISS (England). Phase purity and crystalline patterns for Co nanostructures were studied using X-ray diffractometer (XRD) Bruker Advance D8 XRD, (Germany) (Cu α source with 1.5406 wavelength), in powder mode.

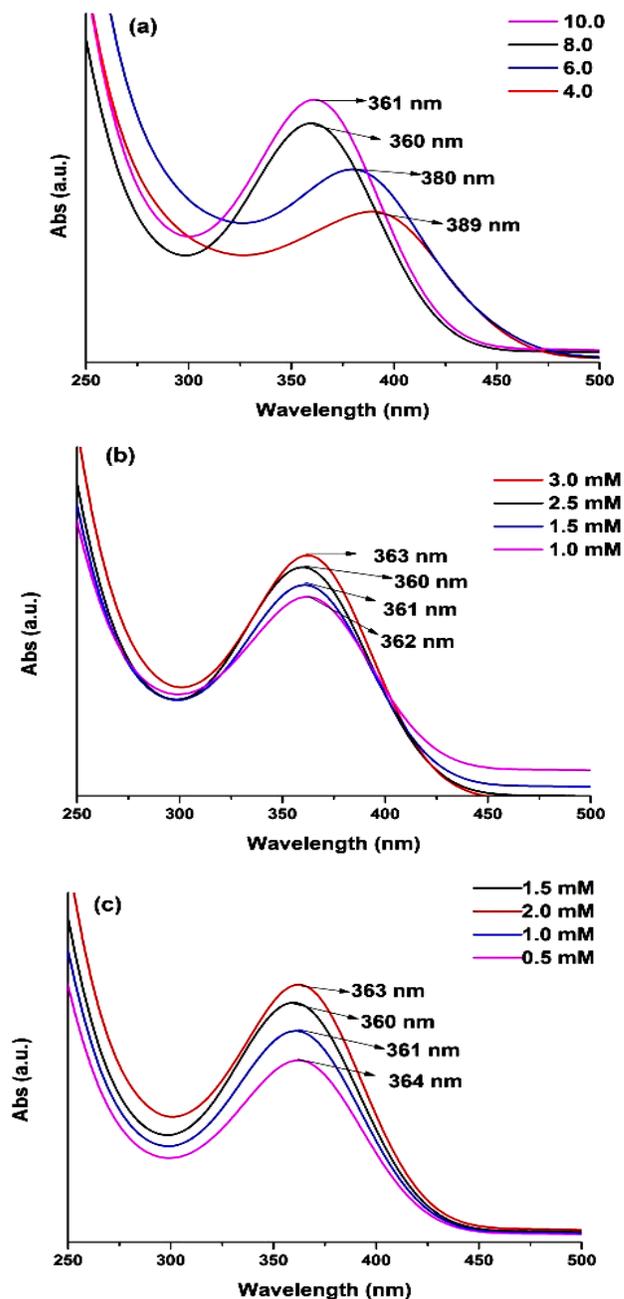


Fig. 1. UV-visible spectral profile for optimization of various reaction parameters (a) pH of colloidal Co NSs (b) Gallic acid and (c) concentration of Co^{2+} ions.

Catalysis study of urchin-like cobalt NSs

In a representative catalytic experiment, specific amount of Co nanostructures (1mg) were deposited on pre-weight

glass cover slips and dried over hot-plate for complete adhesion to surface. These cover slips with specific amount of copper nanostructures were further used in heterogeneous reductive degradation of model nitro aniline (4-methyle-2-nitroaniline). For an un-catalyzed reaction, a solution of 0.3 mM model compound was taken in a 4 mL capacity quartz cuvette along with 10 mM of (NaBH_4) reducing agent. The reaction mixture was studied for some time with an UV-vis spectrophotometer at room temperature and atmospheric pressure. In a similar manner for catalyzed reaction, glass cover slips with appropriate amount of Co nanostructures were placed inside the sample container, previously containing model compound and reductant (NaBH_4) solution. The catalyzed reaction along with kinetics of reaction was followed by measuring the time-dependent fall in absorbance (Abs) at Lambda max of nitro aniline 400 nm.

Recovery and reuse of catalyst

The Co NSs (supported on broken glass cover slips) used in reduction of fresh solution of nitro aniline were removed from the quartz cell, washed 5 times with deionized water and dried. These Co NSs supported pieces of glass cover slips were used in similar way for the reduction of fresh solution of 4-methyle-2-nitroaniline as mentioned in section 2.4. Such treatment was repeated 4 times in order to see any change in efficiency of Co NSs for the given reaction.

Results and discussion

UV-vis absorption spectroscopy analysis

The optical properties of metal nanostructures strongly depend on the particle morphology and size, and thus the changes in shape or size of Co NSs should be reflected by their UV-Vis extinction spectrum. **Fig. 1** shows the UV-Vis spectra for the optimization of various experimental parameters controlled during the synthesis of urchin-like Co NSs. **Fig. 1(a)** represents the effect of solution pH on the optical properties of Co NSs. It can be clearly seen that both the shape and intensity of SPR band for Co NSs changes with the change in solution pH. Since gallic acid has pKa values of 4.1 and 8.38 respectively [24], it was expected to achieve complete reduction above pH 8. The spectral profile clearly demonstrates the blue shift in the SPR band simultaneous with increased intensity and decreased broadness as the pH is raised from 4-10. Interesting, pH = 4 and 6 showed quiet red shifted and very broad SPR band which were observed as a consequence of different morphological shape (spherical) from that of urchin like nanostructures as illustrated in **Fig. 3 (c, d)**. The influence of gallic acid concentration is shown in **Fig. 1(b)**. As expected, raise in concentration of gallic acid allows formation of greater no of nanostructures that result in the blue shift and increased intensity of SPR band. **Fig. 1 (c)** represents the spectral profile for the effect of concentration of precursor salt on SPR band. Continuous increase in intensity with very slight blue shift can be observed with increased concentration of Co^{+2} . This clearly indicates higher nucleation rate as greater no of Co^{+2} per unit area are available. However, at much greater concentration (in this

case 2.0 mM), a red shift in SPR band was observed directing towards growth of nanostructures.

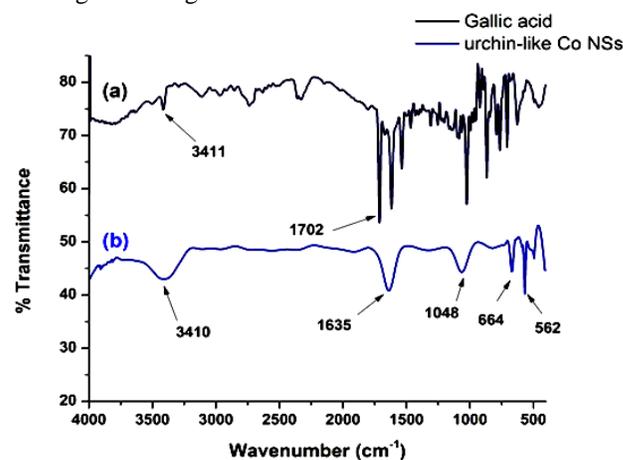


Fig. 2. FTIR spectra of (a) pure Gallic acid and (b) newly synthesized Urchin-like Co NSs.

FTIR study of urchin-like cobalt NSs

FTIR spectra of gallic acid and gallic acid capped Co NSs are shown in **Fig. 2**. FTIR spectrum for standard gallic acid is shown in **Fig. 2 (a)**. Band around $3600\text{--}2500\text{ cm}^{-1}$ with the strong and narrow peak at 1702 cm^{-1} are attributed to stretching vibration of OH group and carbonyl group. Whereas, bands at 1617, 1540, 1451 cm^{-1} are typical stretching vibrations of C–C bonds in aromatic ring of gallic acid. The frequencies are similar to those reported some were else [25]. Several other peaks observed around $1300\text{--}1000\text{ cm}^{-1}$ are attributed to stretching vibrations of C–O bond and bending vibration of O–H bond of gallic acid. In contrast, the shift in stretching frequency of carbonyl group from 1702 to 1635 cm^{-1} shown in FTIR spectrum of urchin-like Co NSs **Fig. 3(b)**, and coverage of C–H stretching vibration around 3100 cm^{-1} by band around $3650\text{--}2700\text{ cm}^{-1}$ of OH group indicated metal surface interaction with functional groups of gallic acid.

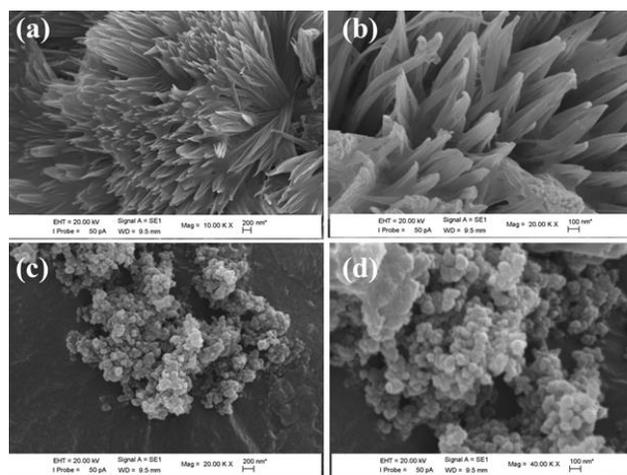


Fig. 3. SEM images of Co NSs (a, b) Urchin shaped morphology obtained at pH =10 and (c, d) spherical aggregates obtained at pH=4 and 6 respectively.

SEM analysis urchin-like cobalt NSs

Fig. 3 shows the SEM images of the as synthesized Co NSs. It can be seen from that all the products consisted of mostly urchin-like morphology with sharp pointed tentacles branched in various directions. **Fig. 3 (a, b)** shows both low and high resolution image of Co NSs revealing dense distribution of urchin tentacles and tapering features of individual structure can be visualized. The Urchin like nanostructures were determined to be about 80-110 nm in diameter with the length of main tentacles between 1.0–1.8 μm . **Fig. 3(c, d)** shows SEM images recorded at pH = 4 and 6 respectively. Morphology obtained at lower pH value were observed to be aggregated spherical particles, based on which we conclude that urchin shaped morphology were constructed via growth of these aggregated particles in random directions.

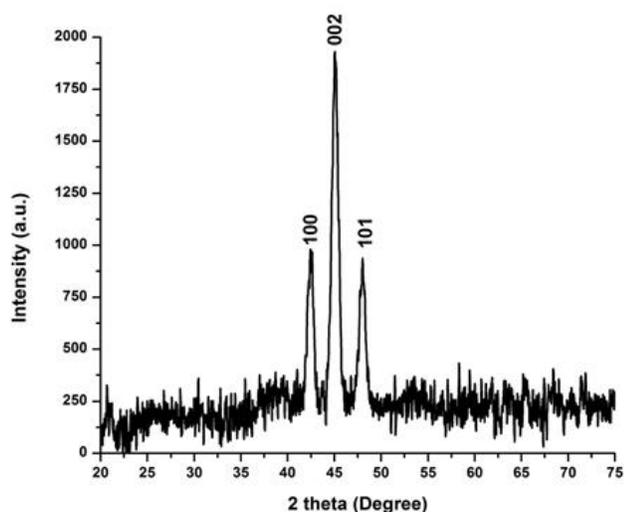


Fig. 4. XRD pattern of Urchin-like Co NSs.

XRD analysis urchin-like cobalt NSs

XRD pattern of urchin-like Co NSs is shown in **Fig. 4**. The phase composition of synthesized nanostructures was identified to be Hexagonal Close-Packed (HCP) phase as indicated by diffraction peaks at $2\theta = 42.5^\circ$, 45.0° , and 48.5° , indexed to (100), (002), and (101) planes respectively. The data was a complete match with the standard diffraction pattern (JSPDC no. 05–0727) of cobalt. Since, it is believed that HCP structure is the most stable phase of cobalt at room temperature [26]. Therefore, data clearly demonstrates formation of stable product with no peaks assigned to oxide of cobalt.

The catalytic activity of Co NSs on the reduction of 4-methyl-2-nitroaniline

The catalytic performance for Co NSs was monitored, taking 4-methyl-2-nitroaniline as a model compound for toxic materials. The chemical formula for is $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$ and the formula weight is 152.15. It is used as a red azo dye and possesses very highly toxic chemical nature [18]. The progression of the reductive degradation of 4-methyl-2-nitroaniline can be easily studied by following decline in time-dependent absorbance at 400 nm as shown in **Fig. 5**.

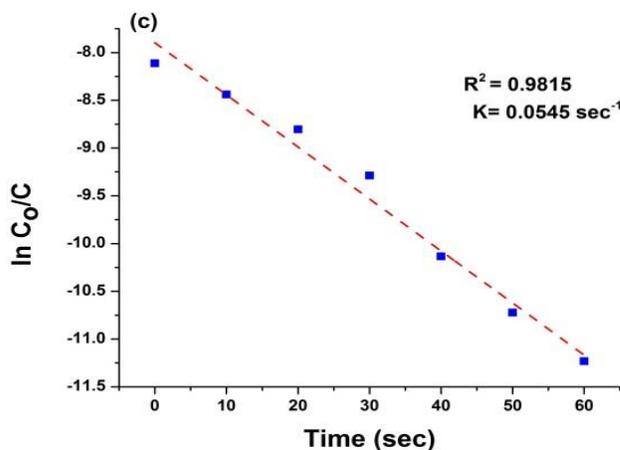
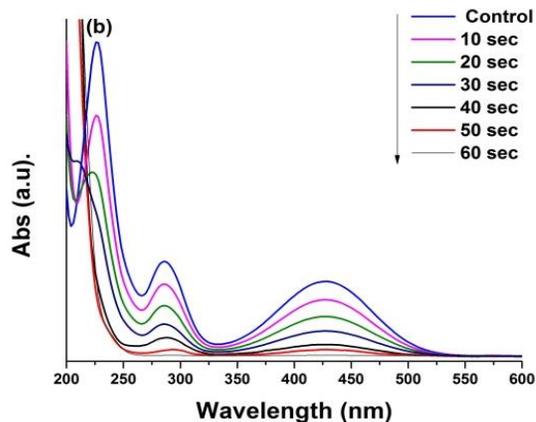
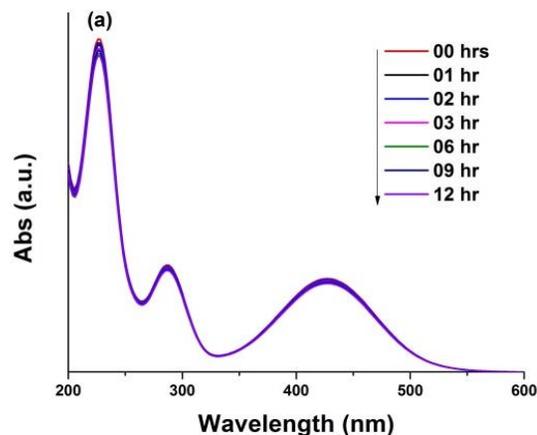


Fig. 5. (a) un-catalyzed reaction carried with 0.3 mM of 4-Methyl-2- Nitro aniline in the presence of 10mM NaBH_4 (b) catalyzed reaction performed with 0.3 mM of 4-Methyl-2- Nitro aniline with 10 mM NaBH_4 and 1 mg of Co NSs (c) Linear regression analysis of pseudo-first order kinetics for the catalyzed reductive degradation.

The un-catalyzed reaction (**Fig. 5(a)**) was carried to assess the capability of reductant NaBH_4 (10 mM) alone with 4-methyl-2-nitroaniline (0.3 mM), which showed only small percentage of degradation (up to 8.5 %) with time. In contrast, catalyzed reaction carried with Co NSs in a similar sample solution suggested the complete reductive degradation of model compound (100 %) within 1 min of reaction time **Fig. 5 (b)**. The rate of reaction for the heterogeneous reductive catalysis of 4-methyl-2-nitroaniline was further described by Langmuir–Hinshelwood (L–H) model, presented in equation (1) [27]:

$$\frac{dc}{dt} \frac{k_{L-H} k_{ad} C}{1 + k_{ad} C} \quad (1)$$

where, k_{L-H} is the reaction rate constant, k_{ad} is the adsorption coefficient of nitro-aniline on catalyst, and C is the variable concentration at any time t . Since for pseudo-first order reaction the value of $k_{ad} C$ is very small as compared to 1 in the denominator of Eq. (1). So integrating equation Eq. (1) for simplification, we obtain

$$\ln\left(\frac{C_0}{C}\right) = k_{L-H} k_{ad} t = -kt \quad (2)$$

Here, C_0 is the initial concentration and $k = k_{L-H} k_{ad}$ is the pseudo-first-order reaction rate constant.

Fig. 5(b) shows the plot with linear relationship of natural logarithm of relative remaining concentration of model compound after reductive degradation versus the corresponding reaction time (s). Rate constant k , for this reaction was found to be $0.055s^{-1}$. The r^2 values calculated from Fig. 5(c) clearly suggest that the removal of 4-methyl-2-nitroaniline fits pseudo-first order kinetics. Although the main process in the degradation of 4-methyl-2-nitroaniline is the adsorption–reduction–desorption phenomena as discussed previously in several studies [28]. However, the detailed mechanism is currently under investigation in our laboratory.

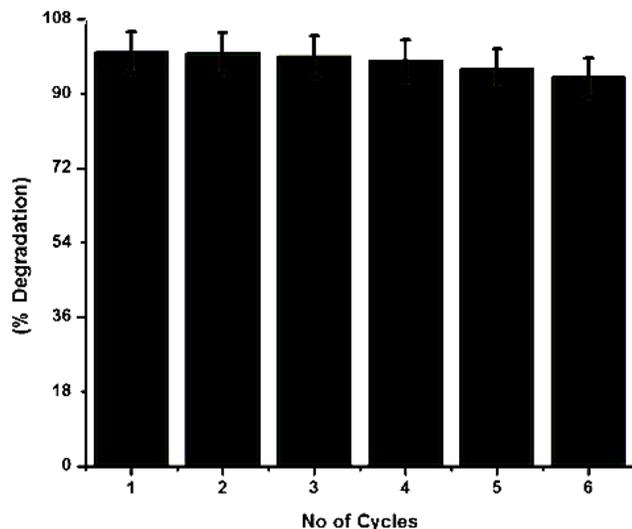


Fig. 6. Bar graph showing the efficiency of Co NSs for the reduction degradation of 4-Methyl-2-Nitroaniline.

Reuse of Co NSs as catalyst

Fig. 6 represents the % degradation of 4-methyl-2-nitroaniline by freshly prepared and 4 times reused Co NSs catalyst with added error bar. The recyclability of catalyst of each sample repeated 5 times to assure the accuracy of result.

The results show excellent catalytic performance of the reused Co NSs and elaborates that the process is highly economized due to high efficiency of the catalyst with negligible poisoning by the solution environment.

Conclusion

In conclusion, greener route was used to synthesized the urchin shaped Co NSs in aqueous solution employing gallic acid as reducing and protecting agent. The approach is simple, cost effective and provides efficient route for preparation of stable Co NSs without the usage of harmful or precarious chemical. Furthermore, the as prepared Co NSs were used as a heterogeneous catalyst for reductive degradation of 4-Methyl-2-Nitro aniline (pollutant). The Co NSs showed efficient catalytic degradation of 4-Methyl-2-Nitro aniline in just 60 sec of total reaction time. Moreover, recovery and reuse of Co NSs with negligible poisoning makes the procedure cost effective and environmental friendly. This work is extendable to the reduction of other phenols as well as other compounds like dyes, and nitrates.

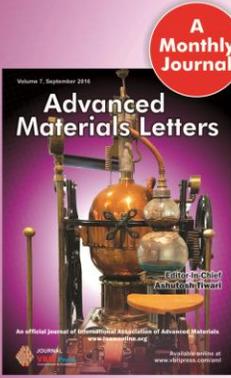
Acknowledgements

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