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ORIGINAL PAPER

Potential of green synthesized zero-valent iron nanoparticles for remediation of lead-contaminated water

R. Kumar · N. Singh · S. N. Pandey

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Abstract A bottom-up green synthesis method has been used to synthesize zero-valent iron nanoparticles taking *Emblica officinalis* leaf extract as reducing and stabilizing agent at ambient temperature and using $FeCl_3$ solution as a source of iron to be reduced. UV–Vis spectroscopy, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction have confirmed the fabrication of green synthesized zero-valent iron nanoparticles. In the UV–Vis spectrum, there was a shift in absorption peak ranging between 350 and 600 nm wavelengths. Nearly, spherical zero-valent iron nanoparticles having average size of 22.6 nm were obtained through this synthesis method. Fourier transform infrared spectrum reveals that the biomolecules are responsible for the synthesis and stabilization of the green synthesized zero-valent iron nanoparticles. Diffraction peak at 2θ of 44.9° in X-ray powder diffraction spectrum illustrates the presence of pure metallic α-Fe nanoparticles with zetapotential value −26.7 mv. With the application of 20 ml l^{-1} concentration, green synthesized zero-valent iron nanoparticles were found very efficient for the remediation of 10, 20, 50 and 100 ppm of lead from aqueous medium within 24 h and the efficiency was positively correlated with the application time period and concentration of GZVINPs.

R. Kumar (✉) · N. Singh
Eco-auditing Group, National Botanical Research Institute, CSIR, Lucknow 226001, India
e-mail: rkumarsagar02@gmail.com

S. N. Pandey
Department of Botany, University of Lucknow, Lucknow 226007, India

Keywords Zero-valent iron nanoparticles · *Emblica officinalis* · Total polyphenol content · Green synthesized zero-valent iron nanoparticles · Zetapotential

Introduction

The present decade witnessed remarkable expansion in the field of nanoscience and nanotechnology because of their wide range of applicability; it deals with the development and application of functional systems (materials) on atomic, molecular or nanometer (10^{-9} m) scale. Nanoparticles are the basic building blocks of this field, where particle size ranges from 1 to 100 nm. Top-down and bottom-up are two general approaches regarding the synthesis of nanoparticles. First one starts with synthesis of nanoparticles through physical method by milling, etching and machining of large size (granular) materials, while the second one starts with synthesis of nanoparticles through chemical and biological methods (atom by atom) by precipitation, positional assembling and self-assembling (Li et al. 2006). So physical, chemical and biological are three main methods regarding the synthesis of different types of nanoparticles (Rao et al. 2004). Although physical and chemical methods may successfully produce pure, well-defined nanoparticles, these require huge amount of energy and are potentially expensive and dangerous due to the involvement of high cost, toxic and flammable reducing agents. Thus as an alternative plant parts (leaf, seed, stem and root), extracts are being utilized for the synthesis of nanoparticles, which is an eco-friendly (green) approach in comparison with physical and chemical methods (Iravani 2011; Njagi et al. 2011). Recently, plant-mediated synthesis of nanoparticles is gaining importance due to its simplicity (can be synthesize in any wet laboratory with least chemicals and instruments), eco-friendliness (no toxic or harmful chemical is used), and now it is emerging as an area of research for large-scale green synthesis of nanoparticles.

Among the various nanoparticles, zero-valent iron nanoparticles (ZVINPs) have gained enormous interest for the remediation of both organic (lindane) and inorganic pollutants (Cr^{6+}) from water and soil due to its small size, large surface area and high reactivity (Elliott et al. 2009; Singh et al. 2011). Ball milling and grinding are the main physical methods through which ZVINPs have been synthesized. Chemically, ZVINPs can be synthesized by using strong reducing agents such as sodium borohydride ($NaBH_4$) (Sun et al. 2007), hydrazine and dimethyl formamide (Raveendran et al. 2003). But plant-mediated synthesis of ZVINPs has been evolved as a method which not only synthesizes but also stabilizes the nanoparticles against aggregation as plant metabolites may act as reducing as well as capping agent for the synthesis of ZVINPs and helps to overcome the concerns related with using $NaBH_4$ as a strong reducing agent, a highly corrosive and toxic chemical (Hoag et al. 2009; Iravani 2011; Shahwan et al. 2011).

Lead is a naturally occurring heavy metal found in trace amount within the earth crust, while the anthropogenic sources include manufacturing of pesticides and fertilizers, fly ash, dumping of municipal sewage, burning of fossil fuels containing lead additives, smelting, mining, paint and battery industry (Henry 2000; Pandey et al. 2009; Singh et al. 2013). Waste effluents of these industries are the main culprit for lead contamination of water as these possess 200–500 mg l^{-1} concentrations of lead (Saka et al. 2012). EPA has included the lead in the list of carcinogenic substances in spite of this several disorders related with gastrointestinal tract, brains, kidneys and central nervous systems are caused by lead in human beings, that is why remediation of lead from industrial waste effluents before discharging them becomes very necessary (Kamaraj et al. 2013).

In all the previous studies, chemically synthesized ZVINPs have been used for the remediation of various pollutants (organic/inorganic), while in the present study, ZVINPs synthesized with *Emblica officinalis* leaf extract have been used for the remediation of Pb^{++} from aqueous medium. The objectives of the present work are as follows: (1) synthesization of ZVINPs with leaf extract of *E. officinalis*, a common Amla (Indian Gooseberry) plant species found in India, (2) characterization of the GZVINPs and (3) application of GZVINPs for the remediation of Pb^{++} from aqueous medium. This work was carried out in CSIR-NBRI, Lucknow, Uttar Pradesh, India, in the year 2013–2014.

Materials and methods

Determination of total polyphenol content (TPC)

TPC of the dried *E. officinalis* leaf was determined by international organization for standardization (ISO) 14502-1 method with spectrophotometer using gallic acid as a standard. For estimation of total polyphenol content, 0.2 gm of dried and crushed leaf sample was extracted in 5 ml of 70 % methanol at 70 °C for 10 min with the help of vortex. Sample was cooled at ambient temperature and centrifuged at 1,337 rpm (200 g) for 10 min. This step was repeated, both the extracts were pooled together, and final volume was made 10 ml with cold 70 % methanol. One milliliter of the 100 times diluted sample was taken in test tubes, and 5.0 ml of ten times diluted Folin–Ciocalteu's reagent and 4.0 ml of 7.5 % sodium carbonate solution were added to it. Tubes were allowed to stand at room temperature for an hour, and absorbance of the samples was measured at 765 nm. The TPC was expressed as gallic acid equivalents (GAE) in gm/100 gm (%) material (ISO 14502-1 2005; Anesini et al. 2008).

Synthesis of ZVINPs

Preparation of leaf extract, $FeCl_3$ solution and their mixing

Fresh leaves of *E. officinalis* (Fig. 1) were collected from the CSIR-NBRI garden, washed thoroughly with distilled water and allowed for air drying at ambient temperature. Washed and air dried leaves were cut into small pieces and heated on a water bath in distilled water in a beaker at 90 °C for 25–30 min. After that beaker is removed from

Fig. 1 *E. officinalis* leaves

the water bath, solution is cooled overnight, filtered with Whatman filter paper and stored at 4 °C. Aqueous ferric chloride solution was prepared by dissolving anhydrous $FeCl_3$ salt (96 % minimum assay purchased from Qualigens) in Millipore quality distilled water in a glass amber bottle.

Aqueous ferric chloride solution and Whatman puradisc™ 25 mm 0.2 μm PES filter media filtered *E. officinalis* leaf extract were drop wisely mixed in different ratios (1:3, 1:4, 1:5, 1:6 and 1:7) at room temperature in different vial tubes by stirring. Quick change in the color of the ferric chloride solution from yellow to black indicates the green synthesis of ZVINPs in the form of intense fine black precipitate. The vial tubes were additionally stirred for 10 min for the complete reduction in the ferric ions (Fe^{+++}).

Characterization of GZVINPs

ZVINPs synthesized by *E. officinalis* leaf extract were characterized with UV–Vis spectrophotometer, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectrophotometer, X-ray diffraction (XRD) and zetasizer nano. Prior to characterization with SEM, TEM and zetasizer nano, GZVINPs slurry was homogenously mixed with a probe-sonicator after dilution in distilled water filtered with Whatman puradisc™ 25 mm 0.2 μm PES filter media. While for the characterization with FTIR and XRD, powdered form of the sample was required. So GZVINPs were ultracentrifuged at 35,000 rpm for an hour for their precipitation in the pellet form, which were oven-dried in hot air oven over the night, after which GZVINPs were pulverized with a mortar and pestle and used for analysis. Initially for the confirmation of green synthesis of ZVINPs, *E. officinalis* leaf extract, aqueous $FeCl_3$ solution and GZVINPs slurry were analyzed colorimetrically by measuring the absorbance with UV–Vis spectrophotometer (Thermo Electron Corporation) at various wavelengths from 200 to 600 nm.

SEM and TEM analysis

Prior to analysis with SEM, GZVINPs were five times diluted in distilled water filtered with Whatman puradisc™ 25 mm 0.2 μm PES filter media and ultrasonicated for 20 min. Scanning electron microscope LEO 430 was used with accelerating voltage of 15,000 V and 32,000× magnifications. Before analysis with TEM, GZVINPs were ten times diluted in distilled water filtered with Whatman puradisc™ 25 mm 0.2 μm PES filter media and ultrasonicated for 30 min. Images of GZVINPs were obtained with Tecnai™ G2 Spirit (FEI, the Netherlands) TEM, operated at 80 kV for high-contrast and high-resolution imaging. For determination of the size and shape of the GZVINPs, one drop of the sample was put on carbon-coated copper grid and left for drying after that the grids were observed under the TEM.

FTIR, XRD and zetapotential analysis

FTIR spectrum of powdered form of GZVINPs was recorded with KBr pellet. For this, thin plates of GZVINP samples were prepared by mixing the sample with spectrally pure KBr, after that infrared spectroscopic analysis was performed in the spectral range of 4,000–500 cm^{-1}. Perkin–Elmer RX1 (range 4,000–450 cm^{-1}) infrared spectrophotometer was used to record the spectrum of the sample. XRD analysis of the GZVINPs was carried out with X-Pert Pro XRD system (PANalytical, Almedo, the Netherlands) which uses Cu K_α radiation and graphite monochromator to produce X-rays with wavelength of 1.54 Å. Powdered form of GZVINPs sample was placed in a glass holder and scanned from 20° to 60°, all major species of iron and iron oxides fall under this scan range, and scanning rate was set 2°/min. Zetapotential can be defined as electric charge at the surface of the ZVINPs and in the vicinity of the nanoparticles. Zetapotential of the GZVINPs was determined by the zetasizer nano (Malvern Instruments, UK), which uses a laser in the range of 5 nm–10 μm in liquid medium. Fresh GZVINPs were ten times diluted in distilled water filtered with Whatman puradisc™ 25 mm 0.2 μm PES filter media and ultrasonicated for 30 min before analysis.

Batch experiments for remediation of lead

Batch experiments were performed to remediate the Pb^{++} by using ZVINPs synthesized with *E. officinalis* leaf extract from aqueous medium. For this experiment, different concentrations of lead 10, 20, 50 and 100 ppm were prepared in distilled water by dissolving the analytical grade lead nitrate salt from Merck (99 % min assay). The reason behind selecting the different Pb^{++} concentrations was to investigate the potential of GZVINPs for the remediation of Pb^{++} containing industrial effluents such as paint and lead acid battery (Henry 2000; Singh et al. 2013). Different concentrations of fresh slurry of GZVINPs as 2, 5, 10 and 20 ml l^{-1} were applied with all the lead concentrations selected for this experiment to check their remediation potential. To evaluate the lead remediation potential of GZVINPs at different time intervals (2, 4, 8 and 24 h), 10-ml water samples were taken from each beaker in different digestion tubes. Solutions were kept on a shaker that was stopped before 15 min of each sampling, and then after sampling, shaker was tuned on again and sampled water were digested with 5 ml conc nitric acid at 150 °C on a hot plate digestion block. Digested water samples were filtered with Whatman filter paper, and final volume of the filtrate was made 25 ml with distilled water and used for lead estimation with AAS (Perkin–Elmer). All the reagents used in this study were of analytical grade, and Millipore quality distilled water was used for the preparation of solutions. All the analyses were done in triplicates, and internal standards and blanks were performed for assurance of quality of the work during Pb^{++} estimation with AAS.

Results and discussion

Estimated total polyphenol content in the *E. officinalis* leaf was found 27.7 % as determined by the ISO 14502-1 method, and most importantly, high polyphenol content and easy availability are the main reasons behind selecting *E. officinalis* leaf as a reducing agent. Polyphenols present in the plant leaves have been reported to control the aggregation and improve the dispersion by acting as a reducing and stabilizing agent (Machado et al. 2013; Wang et al. 2014). When *E. officinalis* leaf extract and aqueous $FeCl_3$ solutions were mixed, color of the solution immediately turns black from yellow and intense fine black precipitates appeared in vial tubes in the form of ZVINPs as observed visually (Fig. 2a). Polyphenol content and ascorbic acid present in *E. officinalis* leaf were thought responsible for the reduction in ferric ions into ZVINPs and stabilization of the GZVINPs (Nadagouda and Varma 2007; Sun et al. 2009; Hoag et al. 2009). Green synthesis of ZVINPs was further confirmed by measuring the absorbance of GZVINPs slurry against the *E. officinalis* leaf extract and ferric chloride solution with UV–Vis spectrophotometer over a series of wavelengths starting from 200 to 600 nm (Fig. 2b). The maximum and similar absorbance for GZVINPs, leaf extract and $FeCl_3$ solution were recorded between 250 and 350 nm, and it was found drastically different after 350 nm.

SEM analysis was carried out for studying the outer surface structure or morphology of the GZVINPs. Micrograph obtained from SEM analysis illustrates uniform and spherical morphology of the GZVINPs (Fig. 3). GZVINPs were found very close to each other because of high concentration and their strong magnetic force. TEM image of the GZVINPs exhibit that iron nanoparticles were found mostly spherical in shape and <100 nm in size (Fig. 4). More than 150 GZVINPs were observed for determining the average particle size, although few aggregates were

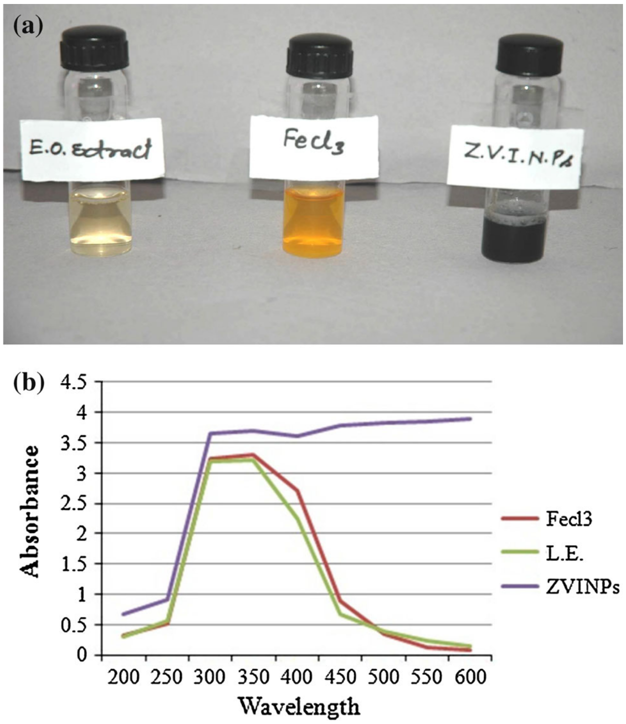

Fig. 2 **a** Synthesis of GZVINPs with *E. officinalis* leaf extract and **b** UV–Vis spectrum of *E. officinalis* leaf extract, $Fecl_3$ solution and GZVINPs slurry

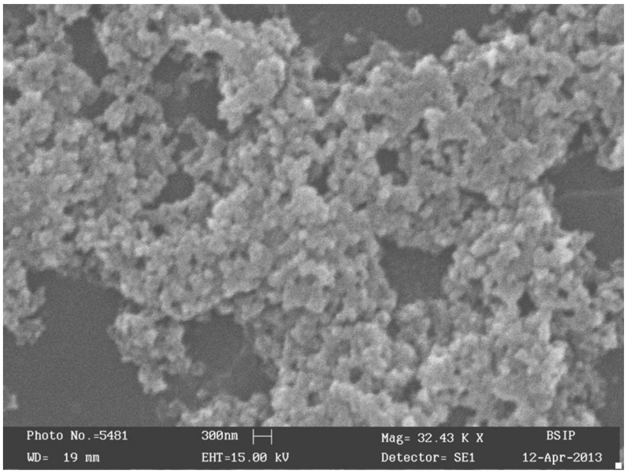

Fig. 3 SEM image of the GZVINPs synthesized with *E. officinalis* leaf extract

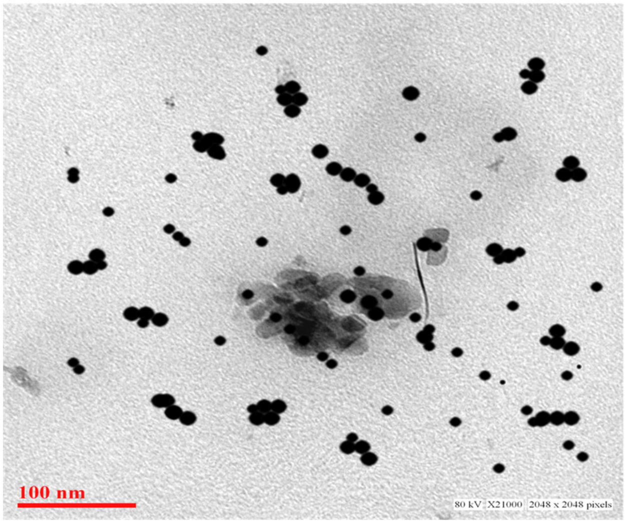

Fig. 4 TEM image of the GZVINPs synthesized with *E. officinalis* leaf extract

also observed but excluding those the average particle size was found to be around 22.6 nm.

FTIR spectroscopy was used to detect the vibrational characteristics of chemical functional groups attached with the sample. Chemical bonds stretch, contract and bend when an infrared light interacts with the sample; as a result, a chemical functional group tends to absorb infrared radiation of a specific wavelength. FTIR spectrum of GZVINPs shows stretching vibrations at 1,616 cm^{-1} for C=C and 1,044 cm^{-1} for C–O–C and O–H adsorption bands at 3,37 and 3,422 cm^{-1}. In the FTIR spectrum of GZVINPs, large stretch of OH functional group and small peaks of others were also observed (Fig. 5a) and these results were found very similar to the results obtained in the study of Wang et al. (2014). XRD analysis was performed to ensure the presence of iron in the sample. The XRD analysis of GZVINPs illustrates that the peak at 2θ of 44.9° indicates the presence of pure metallic α-Fe as a part of GZVINPs, where as some other peaks belonging to oxides of iron, oxyhydroxides of iron were also observed (Fig. 5b). Results of this study were found very similar to the results of Singh et al. (2011). According to the graph obtained from zetasizer nano, zeta (ζ) potential of the GZVINPs was found −26.7 mV (Fig. 5c), which indicates that GZVINPs are moderately stabilized, because nanoparticles with ζ-potential values greater than +30 mV and less than −30 mV are considered maximum stable and started to become unstable as the ζ-potential reaches closer to zero (Zhang and Elliott 2006).

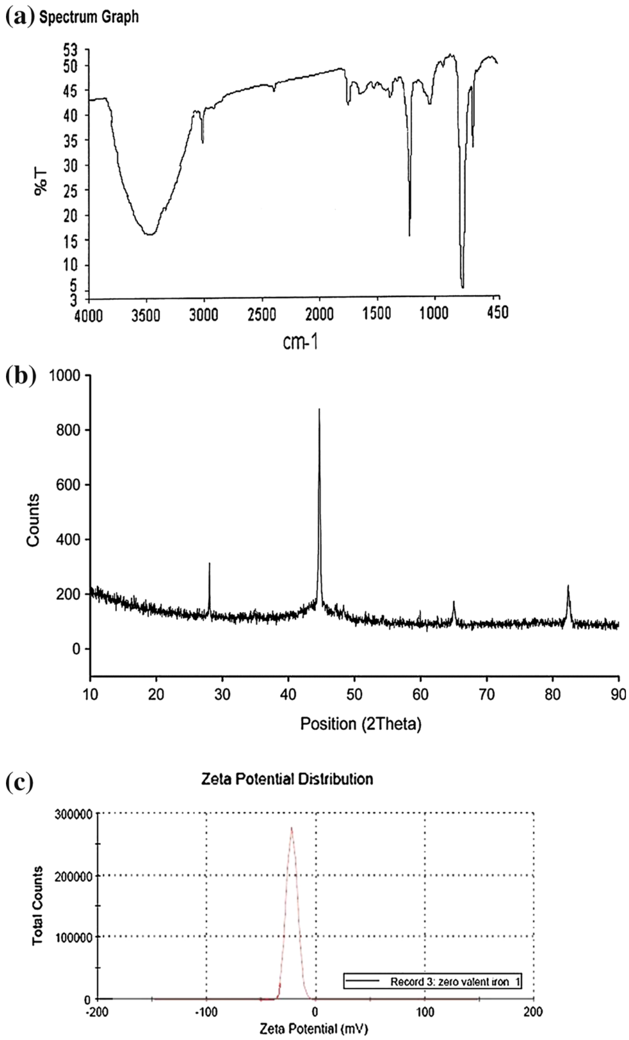

Fig. 5 **a** FTIR spectrum, **b** XRD graph and **c** graph of zetapotential of GZVINPs synthesized with *E. officinalis* leaf extract

To evaluate the lead remediation potential of GZVINPs, batch tests were performed. According to the results obtained from batch tests (Fig. 6), it was observed that there was 80 % reduction from 10 ppm (Fig. 6a) and 15 % from 100 ppm (Fig. 6d) in concentration of Pb^{++} was observed within 2 h, with the application of 2 ml l^{-1}

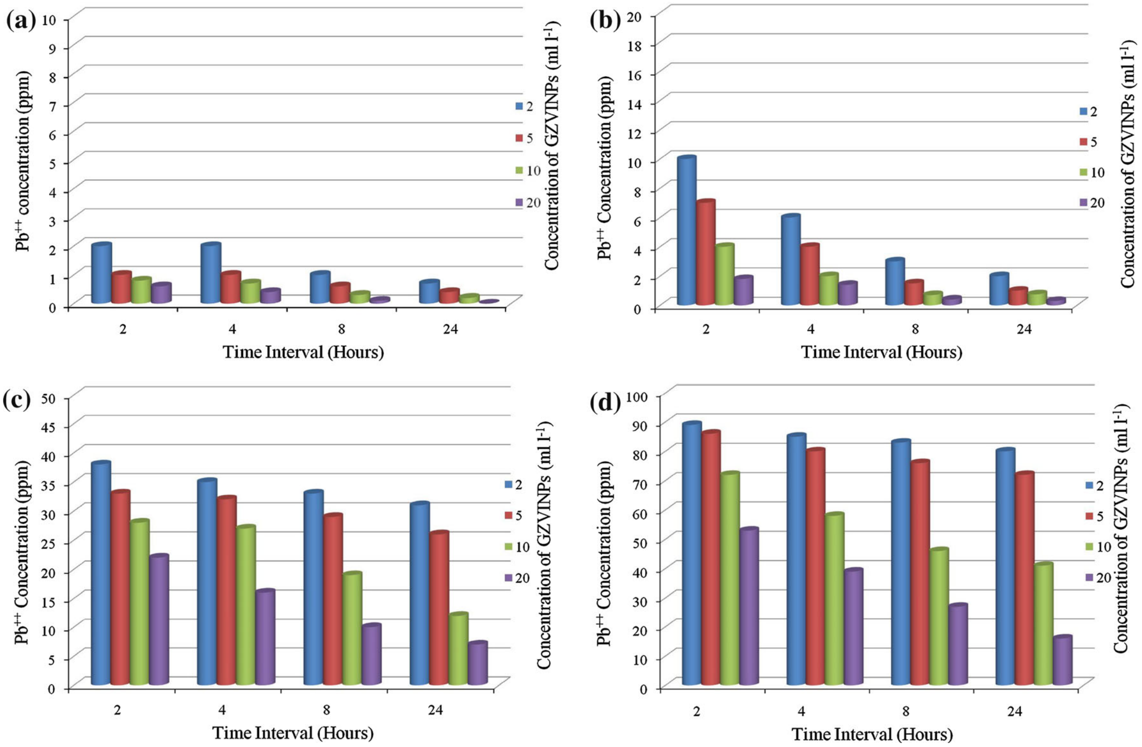

Fig. 6 Remediation of different concentrations of Pb^{++} 10 (**a**), 20 (**b**), 50 (**c**) and 100 (**d**) ppm from aqueous medium at different time intervals 2, 4, 8 and 24 h with 2, 5, 10 and 20 ml l^{-1} concentrations of GZVINPs synthesized with *E. officinalis* leaf extract

concentration of GZVINPs. While with the application of same concentration of GZVINPs, there was nearly about 99 % reduction from 10 ppm (Fig. 6a) and 20 % from 100 ppm (Fig. 6d) in Pb^{++} concentration was observed within 24 h. Moreover, 99 % reduction from 10 ppm and 47 % from 100 ppm in Pb^{++}concentration was found within 2 h, while a higher reduction of 99.9 % from 10 ppm (Fig. 6a), 99 % from 20 ppm (Fig. 6b), 86 % from 50 ppm (Fig. 6c) and 84 % from 100 ppm (Fig. 6d) was observed within 24 h with the application of 20 ml l^{-1} concentration of GZVINPs. When Pb^{++} concentration was low, a lower concentration of GZVINPs and lesser time was required for its remediation, but as the concentration of Pb^{++} increases, low concentration of GZVINPs become insufficient to reduce it. Therefore, a higher concentration of GZVINPs 20 ml l^{-1} along with more time duration (24 h) was required. From the above study, it was observed that the efficiency of GZVINPs is not only dependent on concentration of Pb^{++} and GZVINPs concentration but also on time duration of its application, as the time increases from 2 to 24 h, a higher reduction in the Pb^{++} concentration was observed. The results of this study were found very similar to other results for the remediation of Pb^{++} (Liu et al. 2009; Zhang et al. 2010, 2011). This remediation ability of GZVINPs is due to the combination of adsorption, reduction, oxidation/reoxidation and precipitation processes, which occur on the surface of the ZVINPs at the time of remediation of Pb^{++} (Li et al. 2006; O'Carroll et al. 2013).

Conclusion

On the basis of above study, it can be concluded that the *E. officinalis* leaf extract possess great potential for the synthesis of intensely fine ZVINPs because of the total polyphenol content and ascorbic acid present in it. So toxicity and flammability related issues of using sodium borohydride for the synthesis of ZVINPs were resolved by using *E. officinalis* leaf extract. These GZVINPs at 20 ml l^{-1} concentration exhibit remarkable potential to remediate Pb^{++} present in aqueous medium at 10, 20, 50 and 100 ppm concentrations within 24 h of its application. This ability of GZVINPs offers a significant potential for the remediation of lead and other heavy metals from industrial waste effluents before discharging them into our fresh water streams and in this regard more study is needed.

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Glossary

ZVINPs	Zero-valent iron nanoparticles
GZVINPs	Green synthesized zero-valent iron nanoparticles
TPC	Total polyphenol content
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
FTIR	Fourier transform infrared
XRD	X-ray diffraction

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