Studies on the application of Zirconia nanoparticles for the removal of heavy metal (Pb (II)) from the aqueous solution

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Abstract
In this present study, Zirconia nanoparticles (nanosorbent) have been prepared by both chemical and green methods. The nano sorbent was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) - EDAX and FT-IR techniques. The XRD data revealed the mean crystalline sizes of adsorbent. The surface morphology of adsorbent was studied by SEM. Removal of lead (II) was studied by adsorption of nano sorbent. An unadsorbed lead concentration was found using complexometric titration against standard EDTA with EBT as an indicator.

The factors such as dosage, pH and concentration of Pb (II) were examined to find the efficiency of the process. Adsorption isotherms such as Freundlich and Langmuir isotherm models confirm that the reaction is spontaneous one. Kinetic studies proves that it follows Pseudo-second order kinetic model and was found to be the best fitted model.

Keywords: Lead (II), Zirconia, Nanosorbent, Freundlich, Langmuir, Pseudo-second order.

Introduction

Industrial pollution continues to be a potential threat that alters the nature of water. Heavy metals like Cu, Zn, Ni, Pb, Cd and Cr enter into the water stream and convert the water into a hazardous one. The consumption of polluted water (without treatment) causes various health disorders. Conventional methods for removing Pb (II) ions from industrial wastewater include reduction[4], followed by chemical precipitation, adsorption on activated carbon[12], solvent extraction[13], freeze separation, reverse osmosis[14] and electrolytic methods. Recently, the advancement of nanoscience has shown remarkable potential for remediation of environmental pollution[5]. Nanomaterials are used as novel materials to remove heavy metals ions in wastewater. The novel size and shape-dependent properties of nanomaterials have been investigated[1].

Metal oxide adsorbents include alumina[7], titanium oxide[11], cerium oxide[17] and iron oxide[22] which possesses high surface area and great affinity towards heavy metal adsorption. Zirconia is a neutral bioceramic multifunctional material which exhibits exceptional properties like high chemical resistance, thermal stability and high mechanical property[21]. Zirconium based oxides are stable, non-toxic and high resistant to attack acids and alkalis[9,3]. They are insoluble in water, so they are an attractive choice for the removal in drinking water[2]. The nanostructured Fe (III) – Zr (IV) binary mixed oxide exhibits a good sorption capacity for arsenic removal[6].

The fabricated zirconium oxide nanospheres at high temperature on macroporous ion-exchange media exhibit high adsorption capacity over commercially available iron oxides[8]. The monoclinic or cubic zirconium oxide loaded with porous spherical polymer beads shows the maximum arsenic removal[18]. The concentration of metal ions determined using EDTA complexometric titration was simple, convenient and results are of high precision and accuracy when compared with Atomic Absorption Spectroscopy[20].

In this present investigation, Zirconium nanoparticles prepared by both chemical and biological method were employed in the removal of the heavy metal Pb (II) from its aqueous solution using complexometric titration. The concentration of Pb (II) ions remaining unadsorbed was estimated by titrating the solution against standard EDTA with EBT as an indicator. The optimum dosage, initial concentration of Pb (II) solution, pH and time were found along with the experiment.

Material and Methods

Preparation of *Huberantha senjiana* plant extract: To prepare aqueous plant extract, 50ml of distilled water was mixed with 10 g of *Huberantha senjiana* dried leaf powder and heated in a hot plate with continuous stirring for 30 minutes, cooled and filtered. The filtered plant extract was concentrated and used for further experiments.

Preparation of Zirconia nanoparticles using Chemical method (C.Zr): 0.01M zirconium oxychloride was capped with PVP and stirred. To that solution, add ammonia solution till the pH is raised to 10. The precipitate zirconium hydroxide formed was filtered and washed with distilled water, dried in an oven and calcinated at 400^0C for 2 hours in a Muffle furnace.

Preparation of Zirconia nanoparticles using plant extract (G.Zr): Green zirconia nanoparticles were prepared using the modified procedure[16]. 90ml of 0.01M zirconium oxy chloride was added to 10ml of aqueous plant extract and capped with PVP and stirred. Ammonia solution was added up to pH 10 and stirred. The precipitated zirconium hydroxide was filtered and washed with distilled water, dried in an oven and calcinated at 400^0C for 2 hours.

Preparation of Lead solution: A stock solution (500mg/L) was prepared by dissolving 1.343g of AR grade lead nitrate in 1 L of deionized water. Experimental solutions of the desired concentrations were obtained from stock solution by appropriate dilutions with deionized water.

Characterization of Nanoparticles: UV-Vis analysis was carried out using ELICO SL-159 UV-Vis spectrophotometer to determine the maximum absorption. FT-IR analysis was carried out to determine the functional groups. XRD studies were carried out to determine the structure and SEM – EDAX analysis for surface morphology and composition of nanoparticles.

Methodology: In this present study, removal of Pb (II) on Zirconia nanoparticles was studied. The stock solution was prepared using lead nitrate. The effect of time on the removal rate was tested. Nanosorbent used in this study was weighed and poured in100ml of lead solution and placed in mechanical shaker. The constant concentration of lead was set as 10mg/l at 7 pH and variable time interval of 10 to 60 min. After this time, the adsorbent was removed from adsorbed metal solution by centrifugation.

Finally, the filtrate was titrated against EDTA solution with EBT as an indicator. The amount of unadsorbed lead concentration was calculated from titre values[19]. The experiment was carried out in triplicate. The above procedure was carried out with both nanoparticles synthesized from chemical and green method respectively.

Isotherm models: The mathematical models describe the ratio between the quantity adsorbed and the unadsorbed remaining in the solution at the fixed temperature and the possibility of interaction between adsorbate and adsorbent molecules. To study adsorption process, 1g of Zirconia nanoparticles were added to 1000ml of lead solution with concentrations of 10, 20, 30, 40mg/L. The solution was then mixed at room temperature. The residual concentrations of lead were measured to describe data Langmuir and Freundlich isotherm models were used.

Freundlich Isotherm: It is an important isotherm used to study the equilibrium relationship between adsorbent and adsorbate.

$$Lnqe = lnkf + \frac{1}{n} lnCe$$

where qe is the amount of Pb adsorbed per unit mass of adsorbent (mg/g) at equilibrium, Ce is equilibrium concentration of lead solution, K_f and n are Freundlich constant determined from the slopes and intercepts of the linear plot of $\ln q_e$ versus $\ln C_e$.

Langmuir Isotherm: This is applicable for monolayer adsorption onto the surface of finite sites. The adsorption nature is found to be favorable from calculated R_L value ($0<R_L,1$) from the linear plot Ce versus C_e/q_e:

$$\frac{Ce}{qe} = (1 + bCe)/\ Qob$$

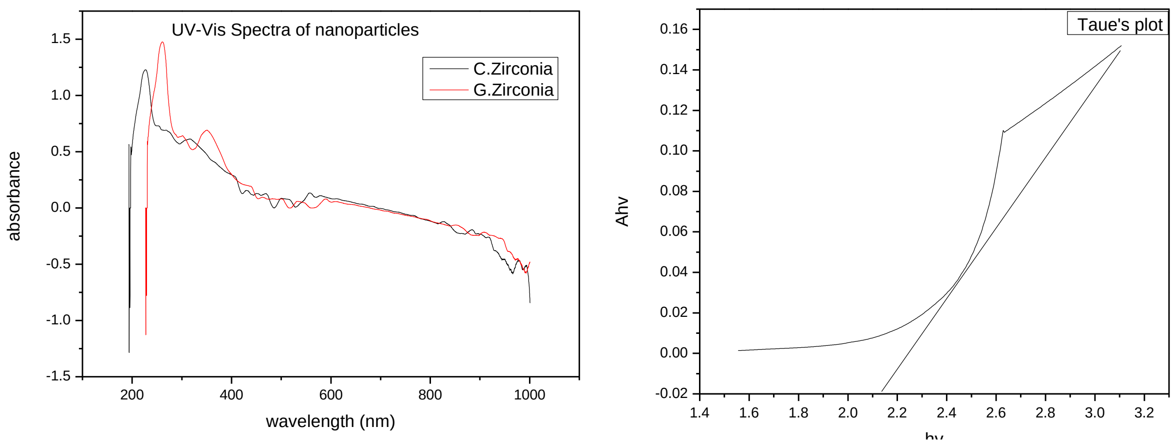
where Q_o and b are Langmuir constants.

Results and Discussion

Characterization of nanoparticles

UV- Vis spectral analysis: The UV-Vis spectra of the aqueous extract and the zirconia nanoparticles showed that the down shift of the wavelength because of the reducing potential of the plant extract. The UV-Vis spectrum of chemically synthesized Zirconia nano particles shows the maximum absorption at 226nm and 264nm and band gap energy using Taue's plot shows 2.14eV. This shows that nanoparticles attained quantum refinement (Fig. – 1a and 1b).

FTIR spectral analysis of Nanosorbent: The IR spectra of nanosorbent show stretching frequency at 3196 cm^{-1} for physically adsorbed –OH with Zr surface. The frequency at 2358 cm^{-1} is due to the coupling effect of both stretching and bending vibration of –OH group. The stretching frequency 1190 cm^{-1} is due to O-H vibration in pure zirconia. The sharp band at 883 cm^{-1} indicates the vibration mode of Zr-O bond (Fig. 2).



(a) (b)

Fig. 1: a) UV-DRS spectra and b) Taue's plot of band gap energy

SEM – EDAX analysis: The Scanning electron micrograph clearly revealed the surface morphology, average particle size distribution and composition of the Zirconia nanoparticles. It was evident from the micrographs that the size of the synthesized nanoparticles was found to be 15 – 20nm in size (fig. 3). The EDAX analysis revealed the composition of elemental zirconium and oxygen signals in Zirconia nanoparticles. The axes display the X-ray electron counts to its energy in KeV. The strong absorption signal of about 2.18 KeV for Zirconia nanoparticles was obtained which is in accordance with the results obtained by Kamal et al[10].

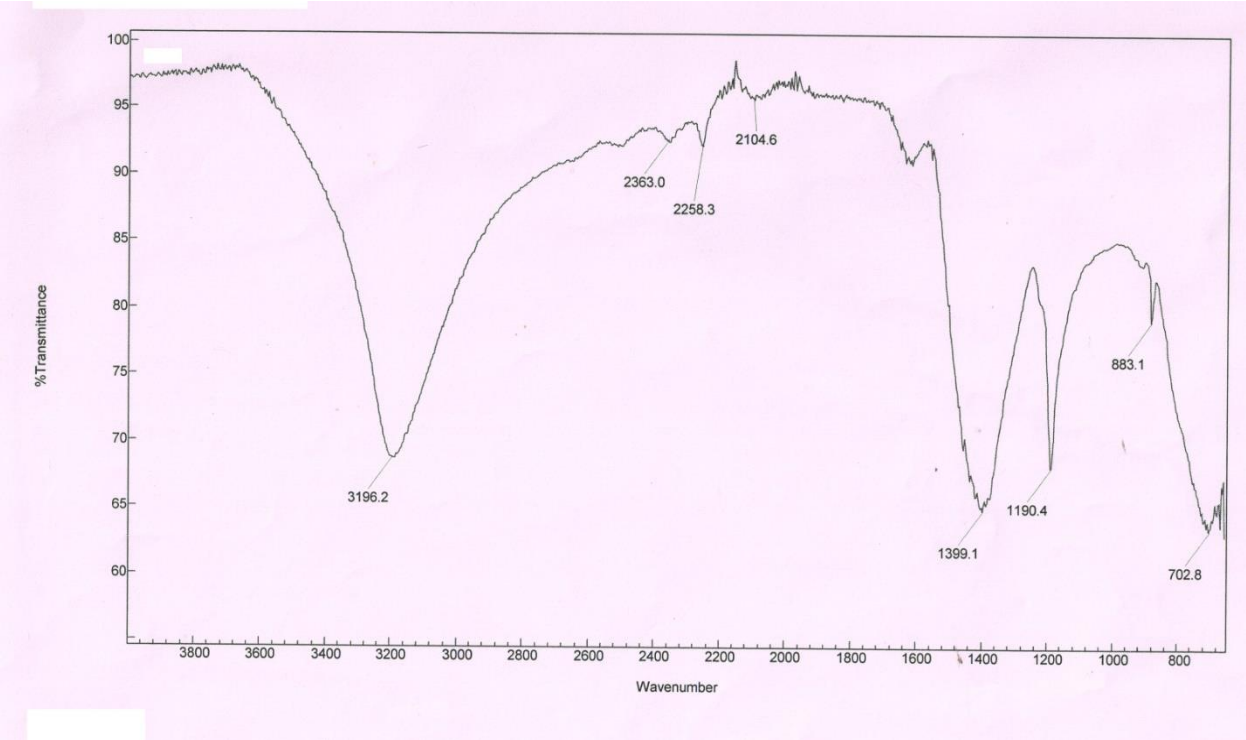


Fig. 2: FT-IR SPECTRA OF ZIRCONIUM NANOPARTICLES

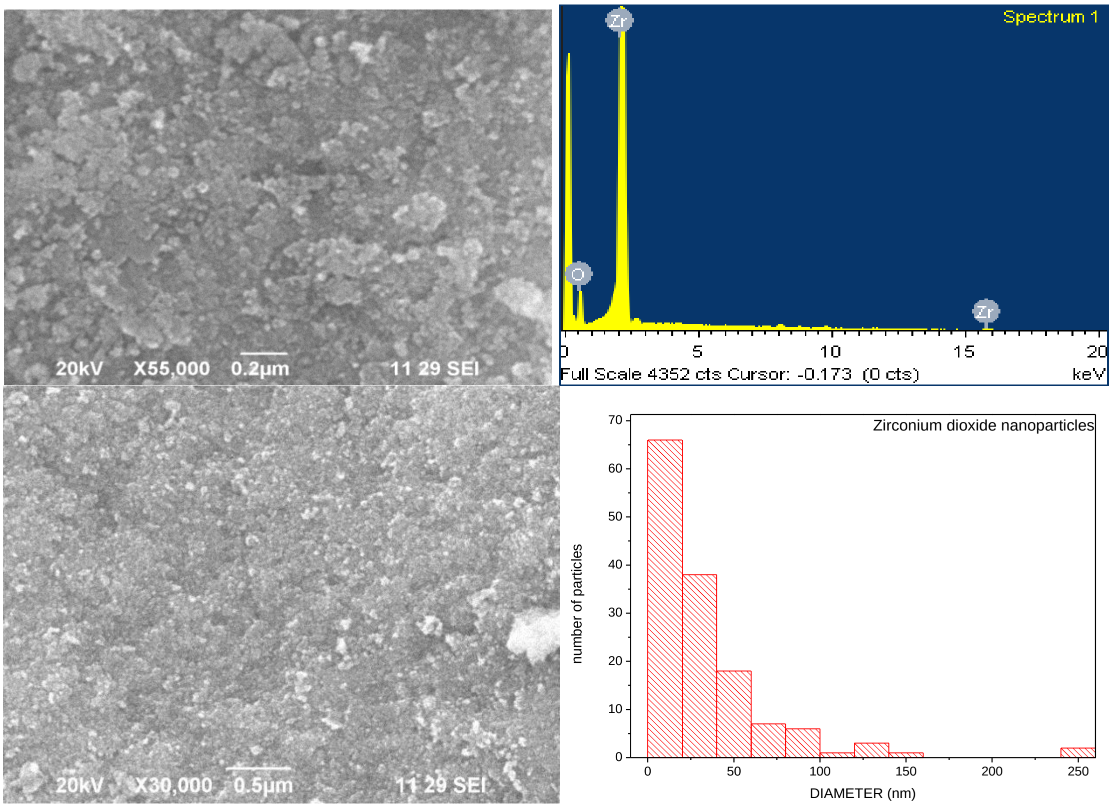


Fig. 3: SEM – EDAX image of zirconia nanoparticles

XRD spectral analysis: The XRD pattern of nano sorbent zirconia is shown in fig. 4. The interplanar distance and intensity values were compared with corresponding standard peaks using JCPDS files. The major diffraction peaks observed at 2θ values are 28.22°, 31.44°, 46.37° corresponding to (110), (113), (126) reflection planes respectively. The XRD pattern of zirconia nanoparticles synthesized from green method shows the similar characteristic peaks as the chemical one. The reflection plane corresponds to the tetragonal phase. The average crystalline sizes of the nanoparticles were found to be 10 to 20nm.The XRD spectra of zirconia nanoparticles synthesized by green method showed the characteristic peaks of tetragonal phase as from chemically synthesized nanoparticles.

The mean crystalline sizes of Zirconia nanoparticles were calculated using Scherrer's formula:

$$D = 0.9\ \lambda / \beta \cos\theta$$

where λ is the wavelength of X-rays (1.540 for CuKα), θ is the Bragg's angle, β is the full width at half maximum.

Adsorption studies: Fig. 5 shows that time is one of the crucial factors affecting the amount of metal adsorbed by the nanosorbent. Nanosorbents have very large surface when compared to other adsorbents. In this study, short time intervals were selected to obtain optimum condition.

The removal of Pb (II) from its aqueous solution increased rapidly during short interval of time 0 – 30 min which is due to availability of large number of free sites on adsorbent surface at the beginning of the reaction. In other words, the less saturating active sites on the adsorbent lead to an increase in rapid speed of collision between metal and adsorbent surface. The green synthesized zirconia nanoparticles show the remarkable removal efficiency.

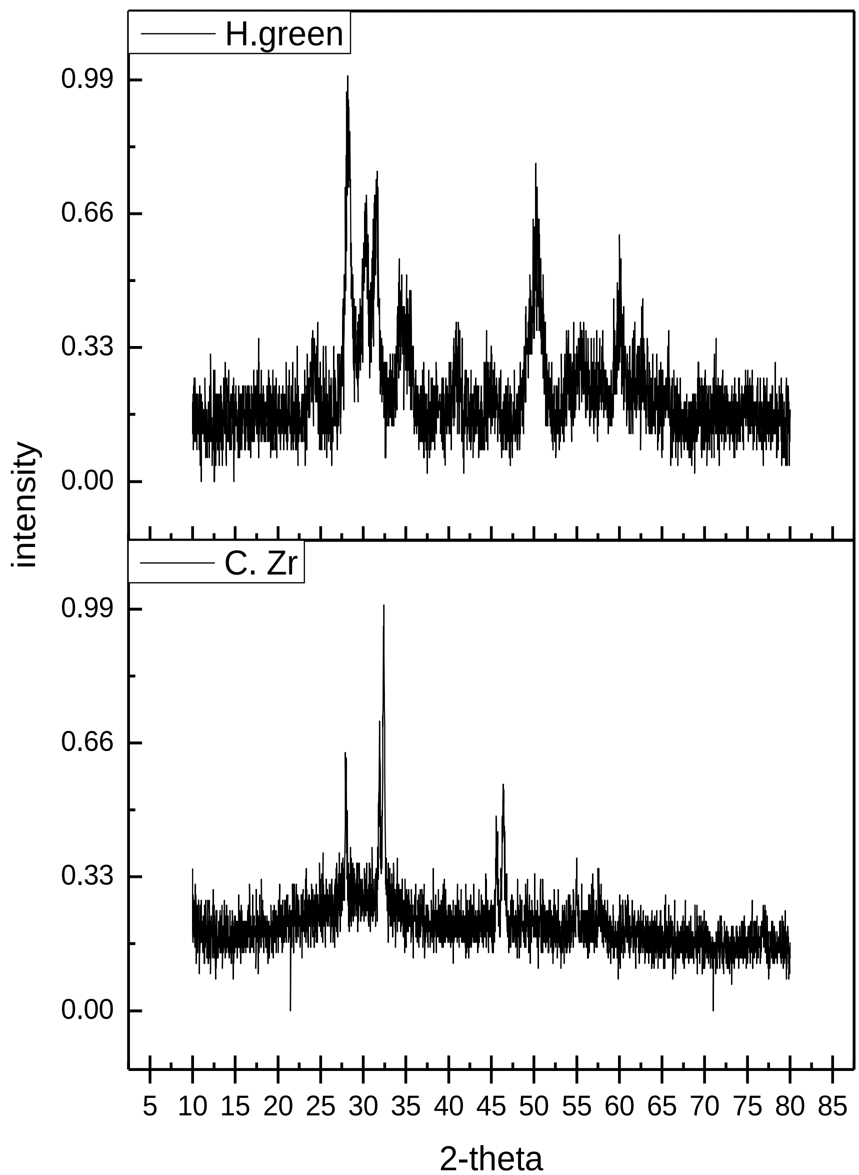


Fig. 4: XRD pattern of zirconia nanoparticles

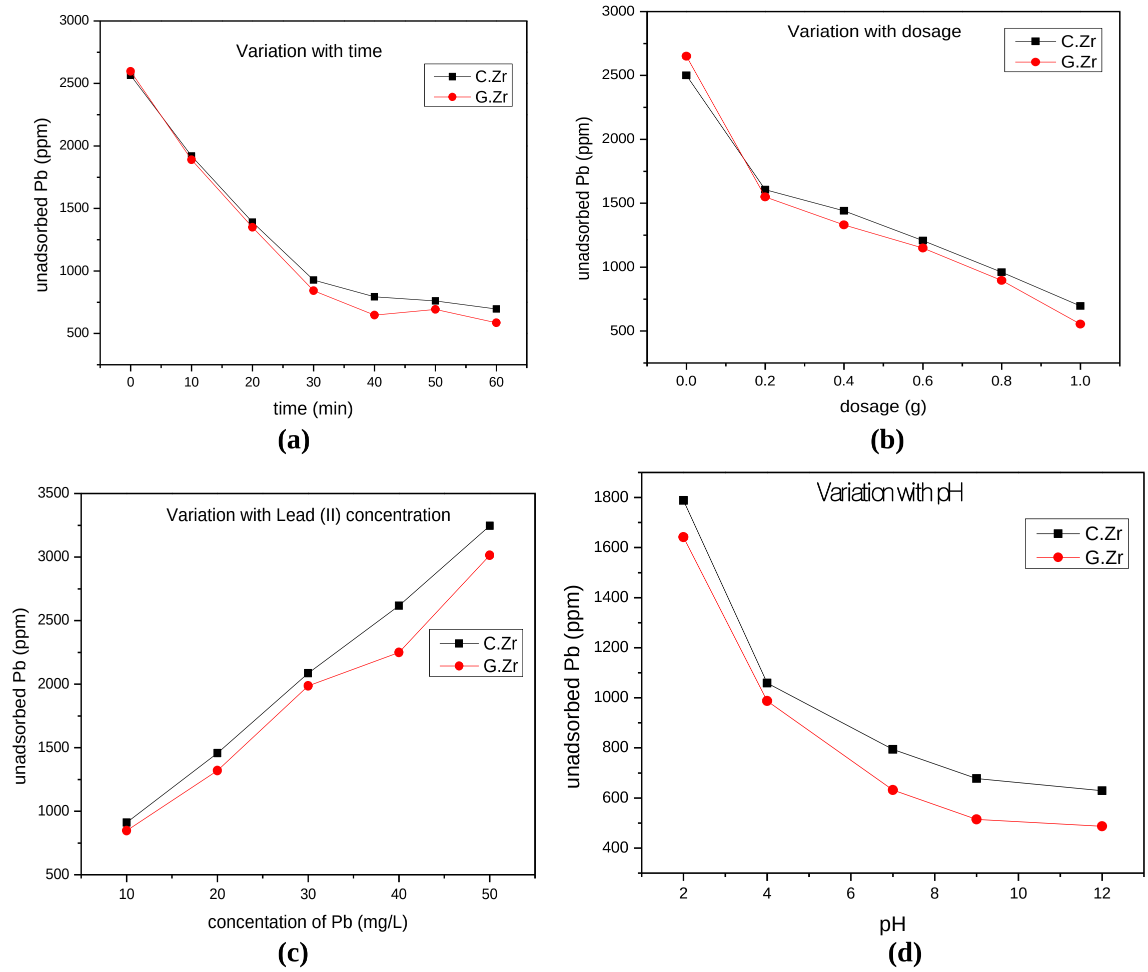


Fig. 5: Adsorption studies of lead in variation with (a) time, (b) dose of nanoparticles (c) initial concentration of lead solution and (d) pH.

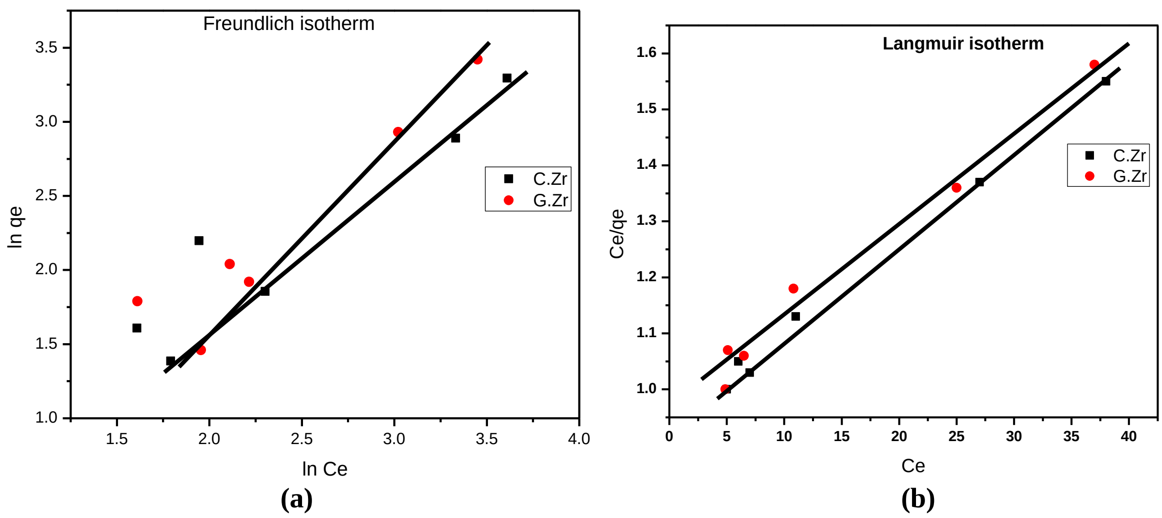


Fig. 6: Adsoption isotherms (a) Freundlich isotherm and (b) Langmuir isotherm

The effect of adsorbent dosage on removal efficiency of metals was observed by varying concentration of adsorbent from 0.2 to 1 g/L. Based on the observation, increasing the concentration of adsorbent increased the removal rate of Pb (II) significantly. This is due to increase in the specific area and probability of collision between particles of adsorbent and ions of metals. The effect of adsorption increases with increase in adsorbent dosage up to dosage 1mg/L and then attains the stability. Hence the effective dosage 1mg/L was found to be optimum.

The effect of initial concentration was studied by varying concentrations of 10, 20, 30 40, 50 mg/L. The removal efficiency reduced with increasing concentrations in which maximum removal of metals was observed at the concentration of 10 mg/L which is attributed to the decrease in thrust force and possibility of low solubility of adsorbent in higher concentration of metal solution.

The maximum adsorption capacity of lead was observed for zirconia nanosorbent at pH 9 which is due to the fact that at high pH values, zirconia is justified because of decreasing H^+ ion concentration in water environment, increasing OH^- and negative anions on adsorbent surface. At high pH values, metal nitrates will have positive loads in aqueous solutions which lead to an increase in adsorption efficiency.

Adsorption isotherms: The isotherm data were fitted well with Langmuir model with higher correlation coefficient (R) which indicated that Pb (II) was chemically adsorbed on the adsorbent surface. Adsorption capacity of lead adsorption was 59.1 mg/g and 61.3 mg/g for both C.Zr and G.Zr respectively. The results are presented in table 1.

Adsorption kinetics- Pseudo-second order model: Kinetics studies for adsorption of lead on zirconia nanoparticles synthesized by both chemical and green method respectively, were performed using pseudo second order kinetic model[15]. The linear form of equation is given as follows:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qe}t$$

The plot t/qt versus t gave a linear fit as shown in fig. 7. The rate constant K_2 and theoretical value of q_e are determined. The correlation coefficient R^2 was almost unity which shows the greater accuracy.

Hence, isotherm parameters and energetic heterogeneity of surface of adsorbent imply the chemisorption process. The adsorption capacity Q_0 was found to be greater for zirconia nanoparticles synthesized via green method. R_L value for both the reactions was found to be less than unity. Therefore, the reaction was found to be spontaneous and feasible. The rate of the reaction of green zirconia nanoparticles was found to be faster than the chemically synthesized nanoparticles and follows pseudo second order.

Conclusion

The biologically synthesized nano zirconia was found to be potent sorbent for the removal of the heavy metal lead from its aqueous solution than chemically synthesized zirconia nanoparticles and does not lead to any secondary pollutant. The major advantage of adopting green synthesis method is to reduce the metal toxicity. The plant extract with potential antioxidants aids the less toxic nanosorbent which in turn is employed for remediation.

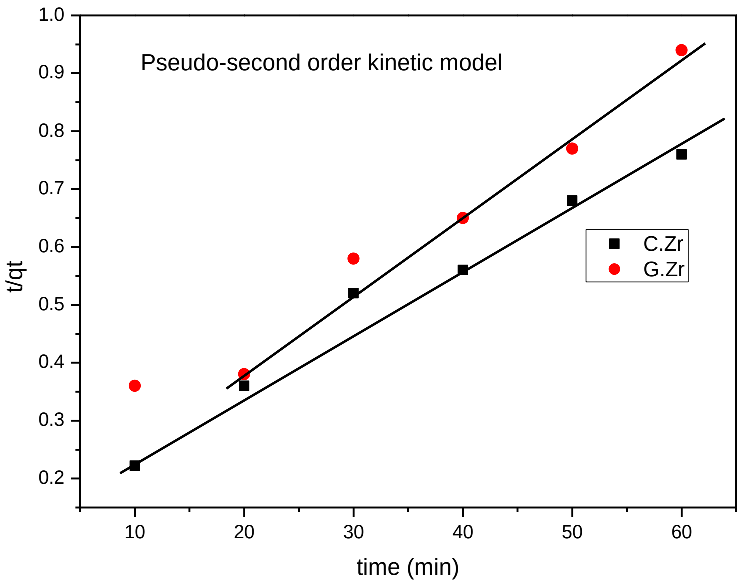


Fig. 7: Pseudo-second order kinetic model

Table 1
Isotherm and kinetic models and their values.

Nanoparticles	**Freundlich Isotherm**		**Langmuir Isotherm**			**Pseudo-second order kinetic parameters**			
	n	**K_f**	**Q_0**	**B**	**R_L**	**Q_e exp (mg/g)**	**Q_e calc**	**K_2**	**R^2**
$C.ZrO_2$ (C.Zr)	1.194	1.4763	59.1	0.0194	0.049	90.2	94.8	$7.1X10^{-3}$	0.998
G. ZrO_2 (G.Zr)	0.975	1.5617	61.3	0.0171	0.0551	88.3	90.9	$5.5x\ 10^{-3}$	0.996

The isotherm data shows that the process is spontaneous and follows chemisorption mechanism. The method adopted for this process is complexometric titration which is cost efficient with high precision and accuracy. Hence, it is concluded that the adopted method was applicable for the removal of heavy metal from the industrial effluent also.

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