

Optimization of Samarium(III) Sorption using Nano-Zirconium Oxide by Taguchi Method

SOM SHANKAR DUBEY^{1,*} and SARIKA GRANDHI²

¹Department of Chemistry, Deen Dayal Upadhyay Gorakhpur University, Gorakhpur-273009, India

²Department of Chemistry, Gitam Institute of Technology, GITAM (Deemed to be University), Visakhapatnam-530045, India

*Corresponding author: E-mail: somshankarbhu@yahoo.co.in

Received: 12 September 2018;

Accepted: 3 December 2018;

Published online: 31 January 2019;

AJC-19268

Sorption of samarium on nano zirconium oxide was carried out as a function of pH, contact time, initial metal ion concentration and temperature. Taguchi's L-25 orthogonal array was adopted to identify the most influential factors accountable for enhanced sorption of Sm(III). In Taguchi analysis the sorption amounts (Q_t) of Sm(III) ions were directed into an precise S/N ratio for a "high is better" response. By examining signal-to-noise ratio (S/N) the quality trail can be determined. The experiment performed under optimum conditions as predicted by Taguchi method resulted in enhanced Sm(III) sorption by zirconium oxide with minimum error. Analysis of variance indicated that the pH of Sm(III) is the most influential factor for high amount of sorption (Q_t). Maximum sorption of 21.3 mg/g (Q_e) was noticed from the solution of initial metal [samarium] ion concentration 0.5 ppm, temperature of 323 K, pH 6.9 and contact time of 50 min [Taguchi optimized factors]. Sorption followed both Dubinin-Radushkevich and Langmuir isotherms. The free energy of sorption was found to be 18.3 kJ mol⁻¹. Pseudo second-order equation well fitted for the sorption kinetics. Sorption increased with increase in temperature. Sorption was endothermic in nature. Reichenburg equation was used to explain the diffusion process. The value of ΔG° was also evaluated. X-ray diffraction and high resolution transmission electron microscopy data supported that the size of the sorbent as 15.5 nm.

Keywords: Samarium, Taguchi, S/N ratio, Isotherm, Thermodynamics.

INTRODUCTION

Tons of millions of wastewater generating annually from various domestic and industrial activities [1]. Thus recycling of waste waters to various levels for benefits like agriculture, construction *etc.* can minimize the inadequacy and can minimize their distraction/diversion from the ecosystem and can maintain the sustainability. Water constitutes two types of pollutants (i) organic and (ii) inorganic pollutants. Metallic pollutants come under inorganic pollutants which were released due to various industrial and acid mine drainage [2]. Recovery can be performed by various techniques like membrane filtration, solvent extraction [3], sorption [4], evaporation, electro dialysis *etc.*, but sorption was chosen as the recovery technique because of its simplicity in procedure and principal, cost effectiveness and low skill and it was an ultimate answer to the water treatment technologies in terms of its purification and recovery procedure [5].

Finding a cost effective recovery process is still under way for the recovery of rare earth elements. Recovery of samarium

from various acid mine drainages, because of high abundance of up to 8.15 mg rare earths per litre, which was a number of orders of magnitude higher than that of the natural water bodies, industrial waste waters and from end on life products is important since the samarium recovery from primary ores generating unnecessary and harmful wastes depending on the source of their primary ore [6]. Till date there is no proper procedure for the recovery of the samarium. Green economy should be found in generating the samarium. Present synthetic batch experimentation is one of the trails in recovery of samarium and to interpret the removal efficiency of the samarium from synthetic dilute solutions of simulated industrial wastewater [7].

Samarium recovery is important since it has immense applications in the present 21st century such as in the synthesis of high temperature resistant magnets, SmCo [8], in the preparation of infrared rays absorbing glasses [8], in the production off the lasers [9], as a catalysts in various chemical reactions [8], ¹⁵³Sm as pain reliever in the bone cancers [9], used as neutron absorbers in the nuclear reactors [9], in the camera

shutters, flint igniters, in the motors of the aeroplanes, as a component in misch metal, in head phones, in guitar pickups and in ipods [8].

Samarium is the one of the rare earths which in sense not rare since it was the 40th abundant element in the earth's crust with concentration of 6 parts per million (in weight). Ores for the commercial extraction of samarium are monazite sand and bastnaesite. Stable isotopes of samarium includes ¹⁴⁴Sm, ¹⁵⁰Sm, ¹⁵²Sm, ¹⁵⁴Sm. Radioisotopes includes ¹⁴⁷Sm, ¹⁴⁸Sm and ¹⁴⁹Sm [9]. Excessive applications of this samarium made the root cause for their extraction. Worldwide 700 tons of samarium was extracted from their ores yearly with primary mining area in Australia, Brazil, India, Sri Lanka and USA [10]. In general solvent extraction and ion exchange are in use for their extraction from ores [11]. Moreover electrolysis was also in use from their molten chloride with NaCl.

Geological weathering, industrial dispensation of their ores and their end product manufacturing are the chief causes for their passage to the environment [12]. Since these are rare in their concentrated forms and found only in few pockets of the world [13] recovery is the essential step. In addition to the above, more over their presence causes health problems such as eye irritations, skin irritations in the humans [14]. Principal organs kidney and liver and blood streams are the exposed areas [14]. Insoluble forms are harmless whereas soluble forms are little toxic [14].

Present paper focused on studying samarium behaviour in the solid/aqueous, conducting batch experiments for the optimization of the reaction conditions for the recovery of the samarium from its synthetic aqueous solutions whose concentrations were in the range of the 0.5-50 ppm and further designing the equilibrium modelling, reaction kinetics, thermodynamic parameters and co-ion effects during the recovery. From the Taguchi L₂₅ orthogonal array (OA) experiments the optimal conditions pH 6.9, initial metal ion concentration 0.5 ppm, temperature 323 K and time period of 50 min were derived. The sorption capacity (Q_e) at optimal conditions was found as 21.3 mg/g.

EXPERIMENTAL

Taguchi method: Taguchi method is considered for alignment of the top combination of primary process parameters to optimize the objective function with lowest list of experimentations with an orthogonal array [15]. An orthogonal array is a least set of tests with numerous combinations of parameter levels. There were three categories of objective applications namely higher-the-better, nominal-the-best and smaller-the-better. The impacts are regularly raised in terms of signal to noise (S/N) ratio. Investigators [16] have at length used this technique in optimization of parameters in the field of adsorption. Present study include the optimizing the factors (pH, initial concentration, temperature and time) responsible for determining the maximum sorption of Sm(III) on nano-zirconia by the technique of Taguchi.

Samarium nitrate hexahydrate [Sm(NO₃)₃·6H₂O] was used as a source for Sm(III) ions, purchased from Sigma Aldrich. For preparing solutions double distilled water was used. Nitric acid and sodium hydroxide aqueous solutions were employed

to maintain the pH conditions during the reaction, purchased from Merck.

Synthesis of sorbent (nano-zirconia): 1 mol of zirconium nitrate hydrate salt was taken in a beaker to that 1.11 mol of glycine was added. Added minimum amount of water and mixed both thoroughly till the solution becomes clear. Now the beaker was positioned on a hot plate and the heat rose to 300 °C. At this temperature the fine powder of ZrO₂ was produced. During the stages of synthesis solution boils initially and produces huge fumes. The ZrO₂ obtained through this flameless combustion was further calcinated for 2 h at the temperature of 500°C [17].

Sorbent characterization:

X-ray diffraction analysis: Tetragonal zirconia was characterized by XRD, X-ray diffraction instrument Rigaku MINI Desktop X-ray diffractometer; CuK_α line (λ = 0.154 nm), FEG-SEM-EDS, field emission gun scanning electron microscopy-energy dispersive spectroscopy and HR-TEM, high resolution transmission electron microscopy (HRTEM Jeol/JEM 2100).

X-ray diffraction of sorbent is reported in Fig. 1 whose 2θ positions matched with the standard JCPDS file number 79-1771 (tetragonal zirconia). The 2θ values of synthesized tetragonal zirconia are 30.119, 34.918, 50.212, 59.673, 62.617, 73.745. Crystallite size is obtained from Scherrer equation given below in eqn. 1. From Scherrer equation, it was confirmed that the zirconia had the crystallite size of 15.5 nm.

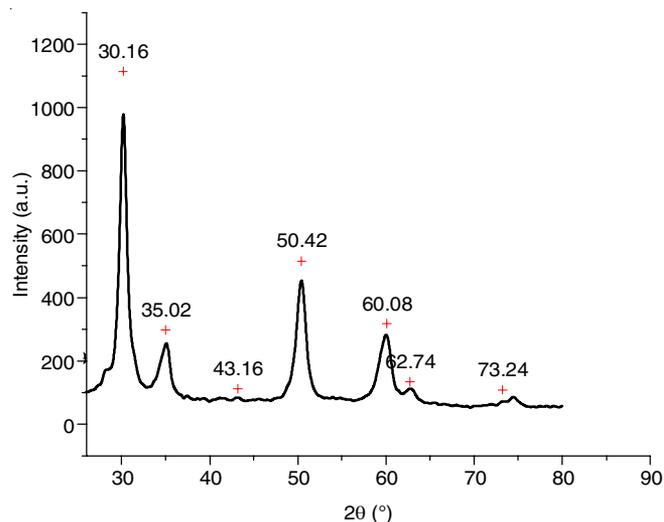


Fig. 1. XRD data of tetragonal zirconia CuK_α line (λ = 0.154 nm)

Scherrer equation:

$$\text{Crystallite size} = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

where λ = X-ray wavelength, B = Full width at half maximum peak of diffraction in radians, θ = Bragg's angle.

FEG-SEM, EDS and TEM analysis: HR-TEM images and FEG-SEM depict the morphology of nano-zirconia shown in Fig. 2(a) and 2(b), respectively. EDS patterns are given in Fig. 2(c). And the post sorption FEG-SEM and EDS is shown in Fig. 2(d) and 2(e), respectively.

FT-IR analysis: Tetragonal nano-zirconia was characterized by FT-IR in the range of 4000-400 cm⁻¹ using KBr disc

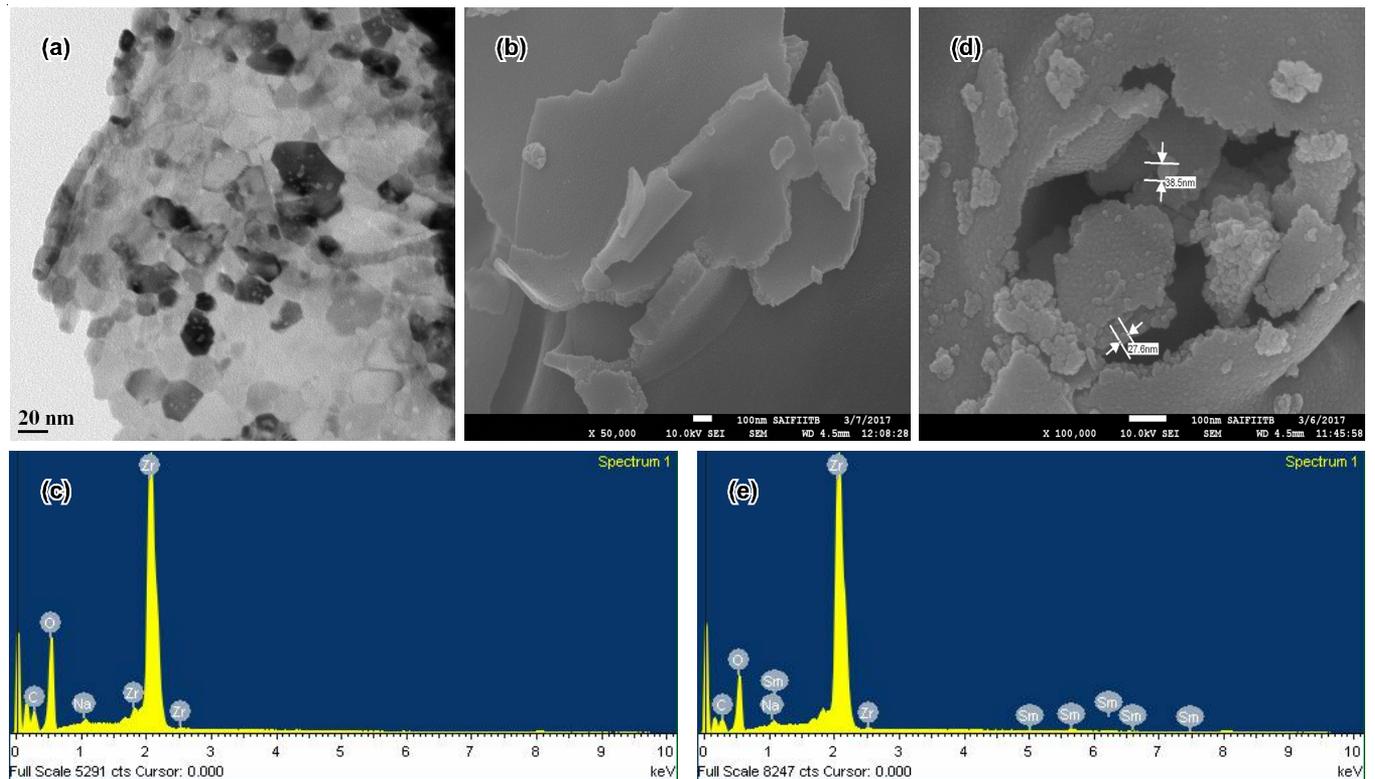


Fig. 2. HR-TEM of (a) nano-zirconia, FEG-SEM of (b) nano-zirconia, EDS of (c) nano-zirconia, FEG-SEM of (d) Sm(III)-nano-zirconia and EDS of (e) Sm(III)-nano-zirconia

method. It displayed bands at 435, 1360, 1520 and 3430 cm^{-1} (Fig. 3a). The detected vibrational band at 435 cm^{-1} assigned to Zr-O bond of tetragonal ZrO_2 . The vibrational band detected at lower frequency region confirms the formation of tetragonal zirconia. Nanomaterials commonly absorb moisture from the atmosphere, for the reason that low intensity peaks of -OH in the FT-IR spectra are observed. FT-IR of zirconia after sorption of Sm(III) displayed shifts in their positions of wavenumbers, deviation in peak intensities, reduction in the broadening of the peaks approves the existence of interaction between zirconia and Sm(III) ions as shown in Fig. 3b.

Selection of sorption factors for Taguchi optimization:

Four factors (initial concentration of sorbate solution, pH of

the solution, time and the temperature) have been recognized for the optimization studies based on our practice. All the four factors have been varied in five levels as shown in Table-1. The design of experiments (DoE) has been carried out based on L_{25} orthogonal array. The combinations for experimental test trails are shown in Table-2. Individual experiment was replicated, to generate the results.

Batch experiment: 1 mg of nano-zirconia was taken in high density polypropylene bottles and 50 mL of samarium sample aliquots of various initial metal concentrations were added and placed in a thermostatic shaker for different time intervals at different pH and temperatures, for the optimization of the reaction conditions by using Taguchi's L_{25} orthogonal

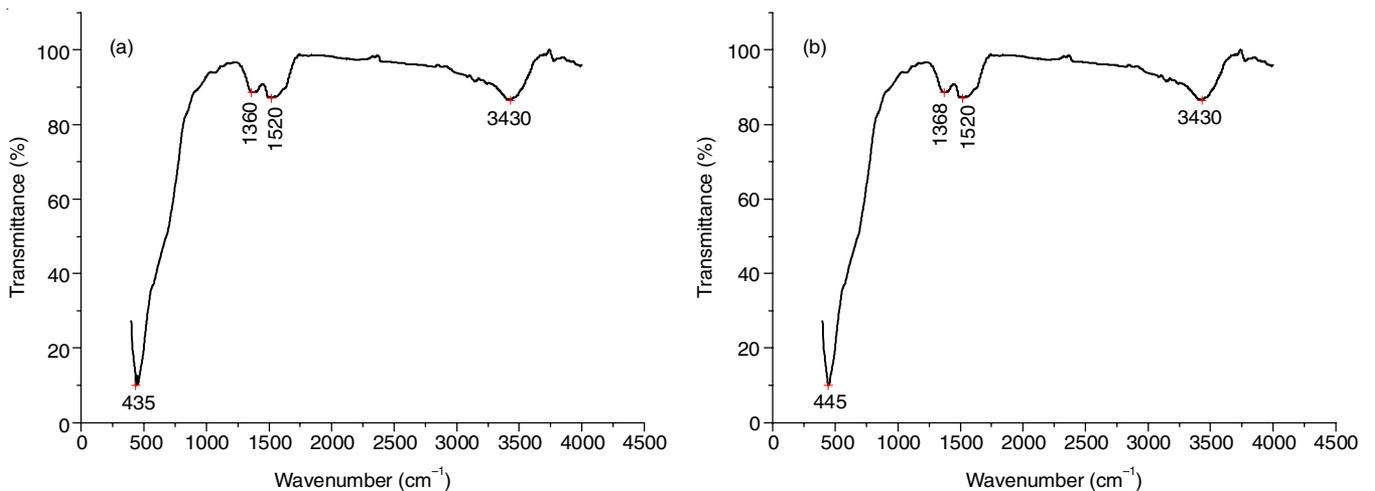


Fig. 3. FT-IR spectra of (a) nano-zirconia, (b) Sm(III)-nano-zirconia

TABLE-1
FACTORS AND THEIR LEVELS

Symbol	Factors	Level 1	Level 2	Level 3	Level 4	Level 5
A	pH	3	4	5.6	6.9	8
B	Concentration (ppm)	0.5	3.6	9	18	50
C	Temperature (K)	273	288	298	313	323
D	Time (min)	20	30	40	50	60

TABLE-2
TAGUCHI'S DESIGN OF EXPERIMENTS
L₂₅ ORTHOGONAL ARRAY

Expt. No.	Factors and levels			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	1	5	5	5
6	2	1	2	3
7	2	2	3	4
8	2	3	4	5
9	2	4	5	1
10	2	5	1	2
11	3	1	3	5
12	3	2	4	1
13	3	3	5	2
14	3	4	1	3
15	3	5	2	4
16	4	1	4	2
17	4	2	5	3
18	4	3	1	4
19	4	4	2	5
20	4	5	3	1
21	5	1	5	4
22	5	2	1	5
23	5	3	2	1
24	5	4	3	2
25	5	5	4	3

array. During the sorption both the phases were separated by centrifugation and the supernatant liquids were collected. The resultant solution concentrations were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES); spectroanalytical instruments GmbH, Germany, ARCOS. The amounts of the sorbed metal ions were calculated from the difference between the initial concentration and final concentration as determined by ICP-AES. The amount of metal ions retained by sorbents at time 't' (mg/g) equilibrium sorption capacity (Q_e) and distribution coefficient (D, mL/g) can be calculated as follows:

$$Q_t = \frac{(C_o - C_t)V}{m} \quad (2a)$$

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (2b)$$

$$D = \frac{(C_o - C_e)}{C_o} \times \frac{V}{m} \quad (3)$$

where C_o , C_t and C_e are the initial, at time 't' and equilibrium concentrations of the samarium ion(s) (mg/L), respectively, V is the volume of the aqueous solutions (mL), m is the weight

of the sorbent (g). The batch experimental results *i.e.*, (Q_e) are given in Table-3. Q_e value is the input objective function, which is needed to be optimized through Taguchi method. Design of experimental factors in Taguchi method would convert the objective into S/N numerical ratio, which is the evaluation index for the quality feature [16]. In this method, the word 'signal' was mentioned as (mean) desirable effect and the word 'noise' was mentioned as (signal disturbance) or undesirable effect of output feature. In the on-going work higher-the-better is selected for Q_e . Occupied relation between S/N ratio and the signal is given by the following equation.

TABLE-3
EQUILIBRIUM AMOUNT OF Sm(III) IONS
AND THEIR TAGUCHI'S S/N RATIOS

pH	Initial conc. (ppm)	Temp. (K)	Time (min)	Q_e (mg/g)	S/N ratios
3.0	0.5	273	20	2.6	8.299467
3.0	3.6	288	30	2.1	6.444386
3.0	9.0	298	40	4.0	12.0412
3.0	18.0	313	50	7.6	17.61627
3.0	50.0	323	60	6.8	16.65018
4.0	0.5	288	40	4.8	13.62482
4.0	3.6	298	50	8.9	18.9878
4.0	9.0	313	60	6.0	15.56303
4.0	18.0	323	20	5.2	14.32007
4.0	50.0	273	30	2.5	7.9588
5.6	0.5	298	60	18.0	25.10545
5.6	3.6	313	20	6.9	16.77698
5.6	9.0	323	30	9.6	19.64542
5.6	18.0	273	40	5.1	14.1514
5.6	50.0	288	50	6.1	15.7066
6.9	0.5	313	30	20.6	26.27734
6.9	3.6	323	40	18.6	25.39026
6.9	9.0	273	50	8.0	18.0618
6.9	18.0	288	60	7.6	17.61627
6.9	50.0	298	20	9.1	19.18083
8.0	0.5.0	323	50	19.1	25.62067
8.0	3.6	273	60	11.6	21.28916
8.0	9.0	288	20	6.1	15.7066
8.0	18.0	298	30	7.1	17.02517
8.0	50.0	313	40	9.0	19.08485

Higher-the-better

$$\frac{S}{N} = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (4)$$

where 'y_i' is equilibrium sorption measured in each experiment averaged over n repetitions, 'n' represents total number of trail runs and 's' represents standard deviation. The relative effect of factors can be obtained from analysis of variance (ANOVA) of S/N ratios.

RESULTS AND DISCUSSION

Taguchi’s S/N analysis of sorption: The L_{25} OA was applied for conducting batch experiments, by using Taguchi method their S/N ratios were calculated and then analyzed. The response table of S/N ratio for Q_e are shown in Table-4. In column 1, the five levels are shown as 1, 2, 3, 4 and 5 and the delta indicates the difference between the highest value and the lowest value. The ranks indicate the order of importance and as first rank for pH, second rank for temperature, third rank for time and fourth rank for initial metal ion concentration. The values are illustrated graphically in Fig. 4, which also illustrates the optimum conditions of sorption.

Level	A	B	C	D
1	21.1	25.13	22.22	23.11
2	22.65	24.18	22.33	22.62
3	25.06	24.08	25.09	24.20
4	26.44	24.12	25.45	25.54
5	25.78	23.53	25.94	25.55
Delta	5.33	1.60	3.71	2.93
Rank	1	4	2	3

ANOVA: The analysis has carried through Minitab 18 software for S/N values to find the influence of the four factors in the adsorption process of the Sm(III) on nano-zirconia. The results of ANOVA are shown in Table-5. pH was the major factor contributing maximum (44.61 %) to Q_e . The contributions from other factors were temperature 27.7 %, time 12.64 %) and the initial metal ion concentration (8.52 %). Table-5

Source	DF	Adj SS	Adj MS	F-Value	Contribution (%)
A	4	295.14	73.785	13.79	44.61
B	4	56.48	14.121	2.64	8.52
C	4	183.98	45.995	8.6	27.7
D	4	83.74	20.935	3.91	12.64
Error	8	42.8	5.35	–	6.46
Total	24	662.15	–	–	100

shows the parameters such as mean of square (MS), sum of square (SS), ratio of mean square factor to the square of error mean (F) and degree of freedom (DF).

Attained optimal conditions: The optimum factors were derived for the evaluation and confirmation for improving the performance of response (Q_e). The optimum factors are selected from the graph of response as A4, B1, C5 and D4, *i.e.* pH: 6.9, Initial metal ion concentration: 0.5, temperature: 323 K and time: 50 min.

Confirmation test: The last step is to predict and validate the Q_e using the optimal level values. The estimated S/N ratio ($\hat{\eta}$) using the optimal level values can be calculated from eqn. 5.

$$\hat{\eta} = \eta_m + \sum_{i=1}^o (\eta_{i_m} - \eta_m) \tag{5}$$

where, η_m denotes total mean S/N ratio, η_{i_m} ; denotes mean S/N ratio at the optimal level and ‘o’ denotes the number of the main design parameters that affect the quality characteristic [18]. Table-6 shows the comparison of predicted Q_e with experimental Q_e using the optimal factors; suitable agreement between the predicted and experimental S/N ratios was observed.

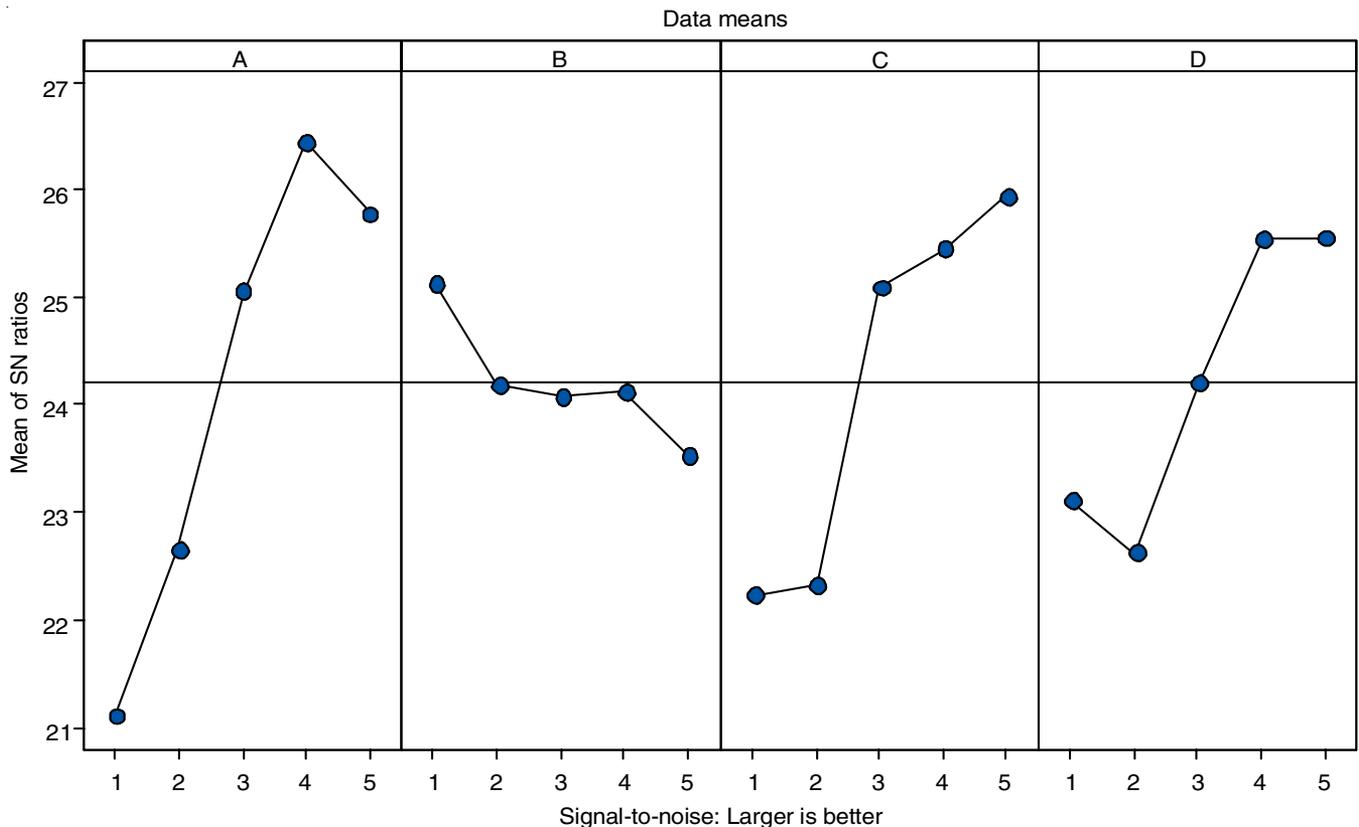


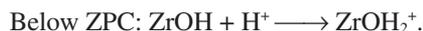
Fig. 4. Main effects for S/N ratios

TABLE-6
RESULTS OF THE CONFIRMATION
TEST AT OPTIMAL FACTORS

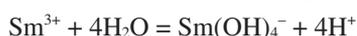
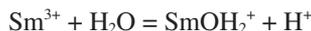
Exp. test	Predicted (S/N)	Experimental (S/N)	Error (%)
26	25.8	27.2	5.1

Effect of initial metal ion concentration, pH, temperature and time: A concentration dependent sorption study of samarium uptake by nano-zirconia was carried in the range of 0.5 to 50 ppm from 273 to 323 K and pH 3 to 8 and time period of 10 to 60 min. It was noticed that, at the lower concentrations of sorption conditions promote uptake of samarium. The reason may be due to the handiness of the relative number of active sites for sorbate. The equilibrium sorption time for Sm(III)-nano-zirconia was 50 min and no prominent uptake was noticed after 50 min. The Q_e value increases by raise in temperature which explains endothermic nature of the reaction. And Q_e increased with increase in pH value and maximized at 6.9. Further increase in pH resulted in the decrease in Q_e .

Mechanism of sorption: Hydrogen ion concentrations play key role in the sorption behaviour of cations on the sorbents. In general at very low pH the sorption of cations will be low due to the competence of the hydrogen ions with the cation of interest. At very high pH the precipitation of the cations will bring into progress. Solid zirconium oxide displays the uncoordinated Zr^{4+} on the surface layer of the solid oxide. When this was dispersed in water the OH^- coordinates with the uncoordinated Zr and results in formation of its hydroxide. This hydroxyl zirconium above its ZPC exhibits negative charge on its surface on deprotonating. This negatively charged surface tends to attract the positively charged Sm species to attain surface neutrality.



Surface interactions of Sm(III) ions with the nano-zirconia studied as a function of pH. Zero point charge of zirconia was 6 [19,20]. Besides ZPC of the sorbent, speciation of the sorbate, which is pH depend. Samarium precipitates from the solution beyond the pH 6.95. At pH 6.9 the major species are Sm^{3+} , $Sm(OH)_2^+$, $Sm^{III}(OH)_2^{2+}$ play prominent role beyond this pH 6.9 which reasons drop of the interfacial contacts between sorbate and sorbents.



Competition of H^+ cations with Sm^{3+} during sorption onto the nano-zirconia (sorbent) may be a reason for the noticed reduction in the sorption at the lower studied pH values (pH < 4.0). The reduction in the sorption efficiency of Sm(III) by nano-zirconia at pH > 8.0 can be due to formation of the SmO_2H (neutral species), which has no affinity towards the active sites (anionic) of the sorbent.

Equilibrium modelling: Equilibrium sorption data of metal ion [samarium] with sorbent [nano-zirconia] for various

initial concentrations (0.5-50 ppm) were modelled using various sorption isotherms at optimum conditions of pH 6.9, temperature 323 K and time 50 min. The sorbent gave straight line and good R^2 value (with samarium) for Langmuir and Dubnin-Radushkevich (D-R) isotherms [10]. Concentration dependent data was utilized for the determination of Langmuir constant (K_L) and sorption capacity (Q_{max}).

Langmuir isotherm equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \quad (6)$$

where Q_e is the amount of metal ions sorbed per unit weight of the solid after equilibrium (mg/g) C_e is the equilibrium concentration of ions remained in the solution (mg/L).

Q_{max} is the maximum sorption capacity (mg/g); K_L is the constant that related to the affinity of the binding sites. Plot between C_e vs. C_e/Q_e gave straight lines (figure not shown). The values of Q_{max} and K_L are obtained from the slope and intercept respectively. A dimensionless constant, equilibrium parameter R_L in Langmuir model brings out the feasibility of the sorption process. R_L values in between 0 and 1 were favourable for sorption.

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

C_0 is the initial concentration of samarium (mg/L). The values of R_L (L/mg) were in the range of 0.00008 (50 ppm)-0.008 (0.5 ppm). The R_L lied between 0 and 1. Therefore, system was favourable for sorption.

D-R isotherm was used to understand the sorption process further.

D-R isotherm:

$$\ln Q_e = \ln Q_{max} - \beta \epsilon^2 \quad (8)$$

where Q_e is the equilibrium amount of samarium that can be sorbed on the oxide, β is a constant related to sorption energy (mol^2/kJ^2) and ϵ is the Polayani potential = $RT \ln [1 + 1/C_e]$ where R is the gas constant in $\text{kJ k}^{-1} \text{mol}^{-1}$, T is absolute temperature in Kelvin and C_e is the equilibrium samarium concentration in solution.

If $\beta < 0$, this relates to the sorption free energy, E, via the relation:

$$E = (-2\beta)^{-1/2} \quad (9)$$

Plot between $\ln Q_e$ vs. ϵ^2 , gave straight lines (figure not shown) for Sm(III)-nano-zirconia. The slope and intercept gave the β and Q_{max} , respectively and the values are reported in Table-7. The values of sorption free energies (E), 18.3 kJ mol^{-1} predict the process as chemisorption [21].

TABLE-7
LANGMUIR AND D-R CONSTANTS FOR
SORPTION OF Sm(III) IONS ON NANOZIRCONIA

Isotherm model	Parameters	Sm(III)
Langmuir	Q_{max} (mg/g)	18.9
	K_L (L/mg)	264.6
	R^2	0.9997
D-R	Q_{max} (mg/g)	20.6
	β (mol^2/kJ^2)	0.0015
	E (kJ mol^{-1})	18.3
	R^2	0.9927

Kinetic studies: Kinetic studies of samarium ion sorption on nano-zirconia was studied at optimum initial metal ion concentration 0.5 ppm, pH 6.9, temperature 323 K and time period of 10-60 min. Kinetics of sorption well fitted in pseudo second-order rate equation and gave linear plots between t/Q_t vs. time. The experimental Q_e close with the calculated Q_e and R^2 close to 1 as reported in Table-8. Sorption rate constant values increased with increase in temperature. This behaviour was noticed in non-physical type of sorption which is conformity with ion-exchange/chemisorption [22].

TABLE-8:
PSEUDO SECOND-ORDER RATE CONSTANTS AND EQUILIBRIUM AMOUNTS OF Sm(III) ION SORBED ON NANO-ZIRCONIA AT VARIOUS TEMPERATURES WITH INITIAL CONCENTRATION OF 0.5 ppm AND pH: 6.9

Temp. (K)	Q_e (mg/g) (experimental)	Q_e (mg/g) (calculated)	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2
323	21.3	21.5	0.007231	0.9894

Pseudo second-order rate equation:

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e} \quad (10)$$

Q_e and Q_t are the amounts sorbed at equilibrium and at time t and k_2 is the sorption rate constant. Linear plots between t/Q_t vs. time. Sorption rate constants (k_2) and equilibrium amounts of samarium sorbed (Q_e) for all studied temperatures have been estimated from the slopes and intercepts.

To predict the mechanism of diffusion kinetic data was used to plot the graph between Bt and t . This Reichenberg plot gave a straight line with an intercept 0.09 confirming the film diffusion [23].

Reichenberg model:

$$F = 1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \quad (11)$$

$$\text{and} \quad B = \frac{\pi D_i}{r^2} \quad (12)$$

$$Bt = -0.4977 - \ln(1-F) \quad (13)$$

F = Fractional attainment of equilibrium at time t

$$F = \frac{Q_t}{Q_e} \quad (14)$$

where Q_t and Q_e are the amounts sorbed after time t and infinite time (24 h), respectively.

D_i = Effective diffusion coefficient of sorbate in the sorbent phase; r = radius of adsorbent particle assumed to be spherical; n = Integer.

Thermodynamic parameters: The thermodynamic parameter ΔG° can be calculated from the following equation:

$$\Delta G^\circ = -RT \ln D \quad (15)$$

For solution of 0.5 ppm (at 323 K) of initial concentration the value of the ΔG° was found to be $-8.6\ kJ\ mol^{-1}$ directs the spontaneity and feasibility of the sorption process.

Effect of co-ions: Sorption efficiency in general, mostly governed on the nature of the sorbate, sorbent and pH. Devia-

tion in any one parameter disturbs the sorption efficiency. Sorption experiments of samarium towards nano-zirconia in the presence of six fold excess of few first, second and third group cations were carried (pH 6.9 for and initial concentration of Sm(III): 0.5 ppm, 323 K). The percentage sorption of the Sm(III) on nano-zirconia in the absence of co-ions was about 85.2 %. On addition of six fold excess of the cations sodium, potassium, magnesium, calcium and aluminium, the sorption was found to be 83.4, 83.2, 80.1, 78.4 and 78.9 %, respectively. The data in Table-9 confirm that the established method has a good tolerance to outward interference and can be applied in the study of high-salinity water samples [24,25].

TABLE-9
EFFECT OF CATIONS ADDED IN SIX FOLD EXCESS IN THEIR CONCENTRATIONS ON THE SORPTION OF Sm(III) ON NANO-ZIRCONIA. [INITIAL CONCENTRATION OF Sm(III): 0.5 ppm; pH: 6.9]

Added cation	Sorbed (%)	Added cation	Sorbed (%)
-	85.2	Mg^{2+}	80.1
Na^+	83.4	Ca^{2+}	78.4
K^+	83.2	Al^{3+}	78.9

Conclusion

Results of this study showed that nano zirconium oxide is effective sorbent for the removal of Sm. The main conclusions of this work are as follows:

- Taguchi method was implemented and the optimal factors were obtained *i.e.*, pH (6.9), initial metal ion concentration (0.5 ppm), temperature (323 K) and time (50 min).
- From the ANOVA results, the contribution percentage of every factor was elucidated. The contribution percentage obtained maximum for pH (44.61 %) and followed in descending order by temperature (27.7 %), time (12.64 %) and initial metal ion concentration (8.52 %).
- A confirmation experiment was conducted to verify the efficiency of the Taguchi optimization method.
- At optimum conditions the adsorption capacity (Q_e) found as 21.3 mg/g.
- The adsorption equilibrium followed Langmuir and D-R isotherms.
- The adsorption process was endothermic in nature.
- Adsorption kinetics followed the pseudo-second-order kinetic model.
- The mechanisms of Sm sorption dominated by chemisorption.

According to the data, prepared sorbent can be considered very promising for the removal and recovery of Sm on account of high adsorption capacity, economic and environmental benign properties.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, GITAM Institute of Technology and Management, Andhra Pradesh, India for providing necessary laboratory facilities and UGC MRP grant (MRP-MAJOR-CHEM- 2013-15298) (F.No.: 43-185/2014-(SR)) dated: 13.02.2016 for funding to carry out the current work. The authors are also grateful to Banaras Hindu

University, Varanasi, India for XRD characterization, STIC, Cochin University, Kochi, India for FT-IR, SEM and HR-TEM and SAIF, IIT Bombay for ICP-AES, SEM analysis.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- J. Kynicky, M.P. Smith and C. Xu, *Elements*, **8**, 361 (2012); <https://doi.org/10.2113/gselements.8.5.361>.
- H. Sun, F. Zhao, M. Zhang and J. Li, *Environ. Earth Sci.*, **67**, 205 (2012); <https://doi.org/10.1007/s12665-011-1497-7>.
- C.A. Morais and V.S.T. Ciminelli, *Hydrometallurgy*, **73**, 237 (2004); <https://doi.org/10.1016/j.hydromet.2003.10.008>.
- L. Anastopoulos, A. Bhatnagar and E.C. Lima, *J. Mol. Liq.*, **221**, 954 (2016); <https://doi.org/10.1016/j.molliq.2016.06.076>.
- C.W. Noack, D.A. Dzombak and A.K. Karamalidis, *Environ. Sci. Technol.*, **48**, 4317 (2014); <https://doi.org/10.1021/es4053895>.
- P.P. Haridasan, P.M.B. Pillai, R.M. Tripathi and V.D. Puranik, *Radiat. Prot. Dosimetry*, **131**, 217 (2008); <https://doi.org/10.1093/rpd/ncn170>.
- T. Dutta, K.-H. Kim, M. Uchimiya, E.E. Kwon, B.-H. Jeon, A. Deep and S.-T. Yun, *Environ. Res.*, **150**, 182 (2016); <https://doi.org/10.1016/j.envres.2016.05.052>.
- P. Enghag, *Encyclopedia of the Elements: Technical Data, History, Processing, Applications.*, John Wiley & Sons, p. 485 (2004).
- J. Emsley, *Nature's Building Blocks: An A-Z Guide to the Elements*, Oxford University Press, p. 372 (2003).
- S.G. Chen and R.T. Yang, *Langmuir*, **10**, 4244 (1994); <https://doi.org/10.1021/la00023a054>.
- G. Barakos, J. Gutzmer and H. Mischo, *J. Sustain. Mining*, **15**, 26 (2016); <https://doi.org/10.1016/j.jsm.2016.05.002>.
- N. Das and D. Das, *J. Rare Earths*, **31**, 933 (2013); [https://doi.org/10.1016/S1002-0721\(13\)60009-5](https://doi.org/10.1016/S1002-0721(13)60009-5).
- R.-L. Tseng, F.-C. Wu and R.-S. Juang, *J. Taiwan Inst. Chem. Eng.*, **41**, 661 (2010); <https://doi.org/10.1016/j.jtice.2010.01.014>.
- K.T. Rim, K.H. Koo and J.S. Park, *Saf. Health Work*, **4**, 12 (2013); <https://doi.org/10.5491/SHAW.2013.4.1.12>.
- G. Taguchi, *Introduction to Quality Engineering: Designing Quality into Products and Processes*, Asian Productivity Organization (1986).
- K.K. Yadav, K. Dasgupta, D.K. Singh, L. Varshney and H. Singh, *J. Chromatogr. A*, **1384**, 37 (2015); <https://doi.org/10.1016/j.chroma.2015.01.061>.
- B.S.B. Reddy, I. Mal, S. Tewari, K. Das and S. Das, *Metall. Mater. Trans., A Phys. Metall. Mater. Sci.*, **38**, 1786 (2007); <https://doi.org/10.1007/s11661-007-9219-1>.
- D.P. Selvaraj and P. Chandramohan, *J. Eng. Sci. Technol.*, **5**, 293 (2010).
- M. Kosmulski, *Adv. Colloid Interface Sci.*, **238**, 1 (2016); <https://doi.org/10.1016/j.cis.2016.10.005>.
- K. Szewczuk-Karpisz and M. Wiśniewska, *Appl. Surf. Sci.*, **379**, 8 (2016); <https://doi.org/10.1016/j.apsusc.2016.04.031>.
- V.J. Inglezakis and A.A. Zorpas, *Desalination Water Treat.*, **39**, 149 (2012); <https://doi.org/10.1080/19443994.2012.669169>.
- S.S. Dubey and S. Grandhi, *J. Environ. Chem. Eng.*, **4**, 4719 (2016); <https://doi.org/10.1016/j.jece.2016.11.006>.
- D. Reichenberg, *J. Am. Chem. Soc.*, **75**, 589 (1953); <https://doi.org/10.1021/ja01099a022>.
- P. Liang, J. Cao, R. Liu and Y. Liu, *Mikrochim. Acta*, **159**, 35 (2007); <https://doi.org/10.1007/s00604-006-0708-5>.
- F. Helfferich, *Ion-Exchange*, McGraw Hill: New York, pp. 116-124 (1962).