

Enrichment of indium from aqueous solution using functionalized sorbent

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The present method utilizes styrene-divinylbenzene-based polymeric material containing phthalic acid as chelating agent to concentrate ultra trace amounts of indium ions in aqueous solutions. Sorption behaviour of In(III) ions under static and dynamic conditions onto the new synthetic resin is reported here. Maximum sorption has been achieved from solution with 8 min of agitation time in the pH range 5-8. The lowest concentration for quantitative recovery is 5 ppb with the preconcentration factor 666. The kinetics and thermodynamics of sorption have been studied in detail. The kinetics follows the first order rate equation with the rate constant k , equal to $0.645 \pm 0.05 \text{ min}^{-1}$. The variation of equilibrium constant k_c with temperature between 10°C to 50°C yields values of ΔH $33.7 \pm 1.96 \text{ kJmol}^{-1}$, ΔS $136.9 \pm 6.4 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G_{303\text{K}}$ $-7690 \pm 200 \text{ Jmol}^{-1}\text{K}^{-1}$. The sorption data in the concentration range 5.26×10^{-6} to $2.19 \times 10^{-4} \text{ M L}^{-1}$ In(III) ions follow Langmuir, Freundlich, and Dubinin-Radushkevich isotherms at all the temperatures investigated. The sorption of In(III) ions onto the synthesized resin in the presence of common anions and cations has also been measured.

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Indium is increasingly used in a variety of industries, viz. coating for display screens used in computers and other electronic devices such as cell phones, instrumentation panels, CD players, etc. Inhalation or tracheal instillation of indium compounds causes severe inflammation of lungs and mild adverse reproductive effects¹. The average intake of indium has been estimated² to be 8-10 µg/day.

It is, therefore, very important to develop sensitive method for quantitative determination of ultra trace amounts of indium. Spectrophotometric methods are simple but not sufficiently sensitive. For the direct determination of indium, a number of sensitive instrumental methods (e.g. atomic spectroscopy) are available, which however, can suffer from systematic interferences by matrix. For this reason, a preconcentration step is often necessary. In recent years chelating resins have proved to be very useful in

the separation and preconcentration of metal ions at trace levels³⁻¹⁴. Such resins can considerably improve the method of analysis extending the limit of detection to lower concentration. The present method involves pre-concentration of indium from large volumes of aqueous solution using phthalic acid modified XAD-16.

Experimental

Varian AA-10 Atomic absorption spectrophotometer was used for the determination of metal ions in solution. The pH measurements were made on a digital (inoLab pH level I) pH meter. Gallenkamp (U.K.) automatic shaker with thermostat was used for the batch experiments. Flow of liquid during the column experiments was controlled by peristaltic pump. Thermo Nicolet Avatar was used to record the IR spectra.

All chemicals used were of analytical grade. Stock standard solution of In(III) was prepared by dissolving the appropriate amount of In(III) nitrate in deionized water (conductivity 0.3 µS, pH 6.0), acidified with small amount of corresponding acid.

Amberlite XAD-16 (surface area of 825 m²/g, pore diameter $1.44 \times 10^{-6} \text{ cm}$, bead size 20-50-mesh size) was procured from Fluka, Germany.

The styrene-divinylbenzene copolymer was prepared according to the reported procedure¹⁴. The synthesis involves nitration of XAD-16, followed by the reduction to form an aromatic amine. This amine facilitates the formation of a stable diazonium salt. The diazotized resin was treated with phthalic acid (5 g) taken in 250 mL of 10% NaOH at 0-5°C for 24 h. The modified resin was washed with 1 M HCl and then with de-ionized water to remove the acidity.

CHN analysis: Found C, 61%, H, 3.9%, N, 8.88%; Calculated for C₁₆H₁₂N₂O₄.H₂O: C 61.14%, H 3.821%, N 8.91%.

Static state sorption of In (III) ion

A weighed amount of phthalic acid modified resin was equilibrated with the 20 mL of indium solution ($4.35 \times 10^{-5} \text{ mol L}^{-1}$) maintained at constant pH and ionic strength at 25°C. The resin was filtered and the sorbed metal ions were desorbed by shaking with 2 M HNO₃/HCl and analyzed by flame atomic absorption

spectrophotometer at wavelength 303.9 nm and slit width 0.5 nm using air-acetylene flame at flow rate of 1.5 L min^{-1} .

Dynamic state sorption of In (III) ions

The synthesized resin (500 mg) was slurried in water, and then poured into a glass column (5 mm $\times$ 50 mm). A small amount of glass wool was placed to prevent any loss of the resin beads during the sample loading. A solution of metal ion ($8.7 \times 10^{-7} \text{ mol L}^{-1}$) was passed through the column at flow rates $1\text{--}10 \text{ cm}^3 \text{ min}^{-1}$ after adjusting its pH to 1-8 with suitable buffer. After the sorption, the column was washed with water and then 1-2 M HCl/HNO₃ to elute the sorbed metal ions. The concentration of the metal ion was determined by atomic absorption spectrometer in both the column effluents sorbed and desorbed.

The sorbed concentration of In(III) ions onto the functionalized XAD-16 resin was computed using the relation:

$$\% \text{ Sorption} = \frac{A_i - A_f}{A_i} \times 100 \quad \dots(1)$$

where, A_i = Absorbance of solution before sorption; and, A_f = Absorbance of solution after sorption. Triplicate measurements were made during the experiments and precision in most cases is close to $\pm 2\%$.

Results and discussion

TG and IR spectra

The chemically modified resin was characterized by Thermal, IR and CHN analysis before sorption studies. The TG plot of functionalized resin shows two-step mass loss up to 500°C . The 5.6% mass loss up to 115°C in the first step is due to sorbed water and suggests that approximately one water molecule per repeat unit of polymer is present. Second step mass loss starts after 200°C , which indicates the high thermal stability of modified resin.

The IR spectra of phthalic acid immobilized XAD-16 exhibits additional bands at 3000-3500, 1695 and 1260 cm^{-1} , which can be attributed to the carboxylic O-H, C=O, C-O stretching, respectively. The important IR band of the modified resin at 1550 and 1185 are due to the N=N and C-N stretching, respectively, and shows the conversion of XAD-16 to functionalized resin¹⁵.

Static sorption studies

Influence of pH on the sorption of In(III) ion onto phthalic acid immobilized XAD-16 was investigated at fixed concentration of In(III) ion and ionic strength. The results show that increasing contact time leads to an increase in the amount of In(III) ion onto phthalic acid immobilized XAD-16 at all pH values in the range 1-8. This indicates that the sorption process involves the release of H⁺ ions to allow the firm complexation of In(III) ions. Hence, increasing the pH value of the aqueous phase should increase the sorption of In(III) ions onto the modified resin. Sorption remains constant in the pH range 6-8. However, pH 6 was selected for further sorption studies.

The kinetics of the sorption of In(III) ions onto synthesized resin has also been studied for 1-100 min. Sorption is very rapid ($\geq 95\%$) within 5 min, which indicates the diffusion of solute through a hypothetical film or hydrodynamic boundary¹⁶. The sorbed concentration at time t , $q_t (\text{mol g}^{-1})$ is plotted against t to test the Morris-Weber equation¹⁷:

$$q_t = R_d \sqrt{t} \quad \dots(2)$$

Eq.(2) holds good up to 5 min but deviates as the agitation time is increased. From the slope of the plot in the initial stage (Fig. 1), the value the rate constant of intra-particle transport (R_d), is estimated to be $23.3 \pm 1.55 \mu\text{mol g}^{-1} \text{ min}^{-1}$. The Lagergren equation¹⁸ was tested by plotting $\log(q_e - q_t)$ vs time, t (Fig. 2), where

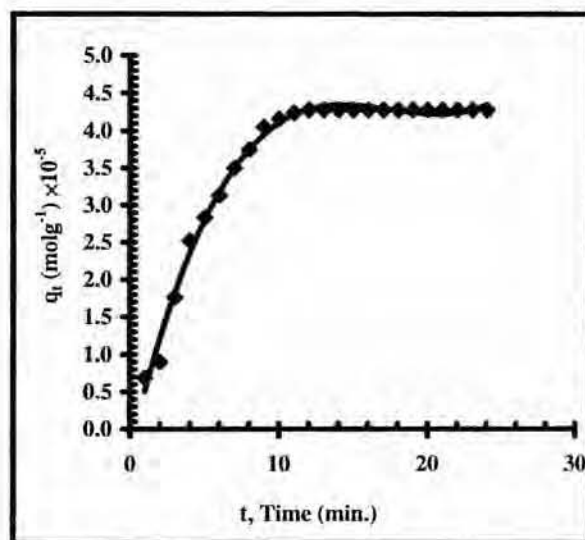


Fig. 1 — Morris-Weber plot for the sorption of In (III) ions on modified XAD-16 resin.

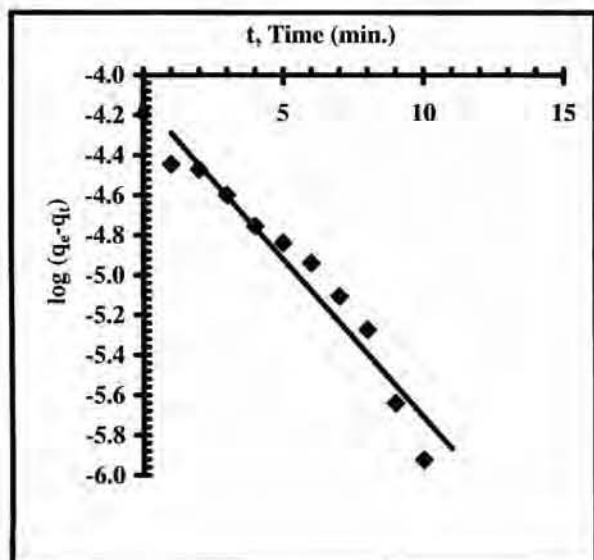


Fig. 2 — Lagergren plot for the sorption of In (III) ions on modified XAD-16 resin.

q_e is the sorbed concentration of metal ions onto modified resin (mol g^{-1}).

$$\log(q_e - q_t) = \log q_e - \frac{K_t}{2.303} \quad \dots(3)$$

In the initial stage up to 4.5 min (Fig. 2), the plot appears to be linear and the slope gives the value for overall rate constant k $0.645 \pm 0.05 \text{ min}^{-1}$.

The effect of temperature on the sorption of In(III) ions onto modified XAD-16 was studied in the range $10\text{--}50^\circ\text{C}$ at optimum conditions. $\ln K_C$ was plotted against $1/T$ (T in K). The values of ΔH , ΔS and ΔG were estimated using the relationships:

$$K_C = \frac{F_e}{1 - F_e},$$

$$\ln K_C = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \text{ and}$$

$$\Delta G = -RT \ln K_C \quad \dots(4)$$

where F_e is the fraction sorbed at equilibrium. From the slope and intercept of the plot, the values of ΔH , $33.7 \pm 1.96 \text{ kJmol}^{-1}$ and ΔS , $136.9 \pm 6.4 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G_{303\text{K}}$, $7.69 \pm 0.2 \text{ kJmol}^{-1}$ have been estimated with the correlation factor 0.995. The positive values of ΔH and negative value ΔG indicate the endothermic and spontaneous nature of the sorption.

The sorption of In(III) ions were also investigated as a function of its own concentration at different temperatures in the range of 2.41×10^{-6} to $1.44 \times 10^{-4} \text{ mol L}^{-1}$ using 100 mg sorbent and 10 min shaking time at a shaking speed of 30 rpm. The initial rapid sorption gives way to a slow approach to equilibrium at higher sorbate concentrations. The uptake of metal ion is 75–100% at low concentrations and 25–78% at higher concentration. These results reflect the efficiency of resin for the removal and preconcentration of indium from aqueous solution in a wide range of concentration. The uptake of In(III) ions increases with increase in temperature, thereby indicating the process to be endothermic in nature. The sorption data were subjected to different sorption isotherms namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R). The data follow all three isotherms over the entire concentration of In(III) ions and temperature range investigated.

The Freundlich isotherm is the most widely used mathematical model, and gives an empirical expression encompassing the surface heterogeneity and exponential distribution of active sites and their energies¹⁹:

$$\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_e \quad \dots(5)$$

where C_{ads} is the amount of sorbate (mol g^{-1}) and C_e is the amount sorbate in liquid phase at equilibrium (mol L^{-1}), A is a constant related to the sorption capacity and $1/n$ is a constant related to energy or intensity of sorption. The $\log C_{\text{ads}}$ was plotted against $\log C_e$. Langmuir model¹⁹ represents chemisorption on a set of well-defined localized sorption sites having same energy, independent of surface coverage and no interactions between sorbed species. The Langmuir model was tested in the following form:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad \dots(6)$$

C_e is the equilibrium concentration of sorbate in solution (mol l^{-1}) and C_{ads} is the amount of sorbate (mol.g^{-1}) on sorbent surface, Q is the maximum amount of solute sorbed corresponding to monolayer coverage of sorbent surface and b is a constant related to the binding energy of solute. The plot of C_e/C_{ads} vs C_e gives a straight line at all temperatures investigated indicating that Langmuir sorption is also followed by the sorption data very well. The essential characteristic of Langmuir isotherm can be expressed

Table 1—Langmuir, Freundlich and D-R sorption isotherm parameters at different temperatures for the sorption of In(III) ions on modified XAD-16

Temp. (°C)	Langmuir				Freundlich			D-R		
	Q ($\mu\text{mol g}^{-1}$)	$b \times 10^5$ (l g^{-1})	R_L	r	A (mmol g^{-1})	$1/n$	r	X_m (mmol g^{-1})	E (kJ mol^{-1})	r
10	55.8 ± 0.95	3.19 ± 0.7	0.034	0.999	1.51 ± 0.38	0.34 ± 0.021	0.984	0.24 ± 0.018	13.4 ± 0.44	0.980
20	100 ± 4.2	1.92 ± 0.68	0.056	0.994	1.58 ± 0.48	0.29 ± 0.024	0.972	0.48 ± 0.016	13.5 ± 0.35	0.990
30	118 ± 5.3	1.38 ± 0.57	0.058	0.989	6.45 ± 1.6	0.41 ± 0.019	0.989	0.49 ± 0.011	14.0 ± 0.23	0.993
40	147 ± 9.7	1.9 ± 0.66	0.056	0.979	12.0 ± 3.5	0.44 ± 0.023	0.995	1.33 ± 0.019	14.0 ± 0.32	0.990
50	168 ± 8.0	2.9 ± 0.77	0.036	0.989	31.6 ± 14.9	0.49 ± 0.03	0.998	1.50 ± 0.030	13.5 ± 0.37	0.983

r = correlation coefficient

R_L = dimensionless constant when $C_i = 4.8 \times 10^{-5} \text{ Mol L}^{-1}$

in terms of dimensionless constant, Separation factor R_L , which describe the type of isotherm²⁰ and is defined by:

$$R_L = \frac{1}{(1 + bC_i)} \quad \dots(7)$$

where b is Langmuir constant and C_i is the initial concentration of In(III) ions. The values of R_L calculated were between 0 and 1 (Table 1) indicating highly favourable sorption of In(III) onto modified resin at all temperatures investigated.

The Dubinin-Radushkevich isotherm is postulated within an adsorption 'space' close to adsorbent surface¹⁹. The model features the heterogeneity of energies over the surface. The linear form of D-R isotherm, which was plotted, is given by:

$$\ln C_{\text{ads}} = \ln X_m - \beta \epsilon^2 \quad \dots(8)$$

where C_{ads} is the amount of metal ion sorbed and X_m is the total adsorption capacity, β is the activity coefficient having dimensions of energy and ϵ is Polanyi potential which is equal to:

$$\epsilon = RT \ln (1 + 1/C_0) \quad \dots(9)$$

Here, R is gas constant in $\text{kJ mol}^{-1} \text{K}^{-1}$ and T is the temperature in Kelvin. β is related to the mean sorption energy (E)²¹ as:

$$E = \frac{1}{\sqrt{-2\beta}} \quad \dots(10)$$

This is the free energy of the transfer of one mole of solute to the surface of the adsorbent. The saturation limit, X_m , may represent total specific micropore volume of the sorbent. The Freundlich, Langmuir and D-R constants were evaluated using slopes and intercepts of linear plots of both the metal ions studied. The results are listed in Table 1. The numerical value of Freundlich constant $1/n < 1$ shows that sorption capacity is only slightly suppressed at lower equilibrium concentrations.

The value of sorption capacity is different for all three sorption isotherms. This difference in sorption capacity can be interpreted in terms of the assumptions taken into consideration while deriving these sorption models.

Dynamic state sorption studies

Effect of flow rate — The effect of flow rate on the sorption was studied at flow rate $1-8 \text{ cm}^3 \text{ min}^{-1}$ at the pH chosen for maximum sorption. It was observed that at flow rate greater than $3 \text{ cm}^3 \text{ min}^{-1}$, there was decrease in % sorption. Therefore, $3 \text{ cm}^3 \text{ min}^{-1}$ was taken as optimum flow rate.

Recovery studies — Different mineral acids were used to desorb the metal ions from the resin. The efficiency of stripping mineral acids was studied by using different volumes ($1-5 \text{ cm}^3$) and concentration of HCl. It was found that 3 cm^3 of 2 M HCl was sufficient for more than 98% recovery of In(III) ions. Therefore for complete recovery, 3 cm^3 of 2 M HCl was used.

Limit of preconcentration — The limit of preconcentration was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at $10 \mu\text{g}$.

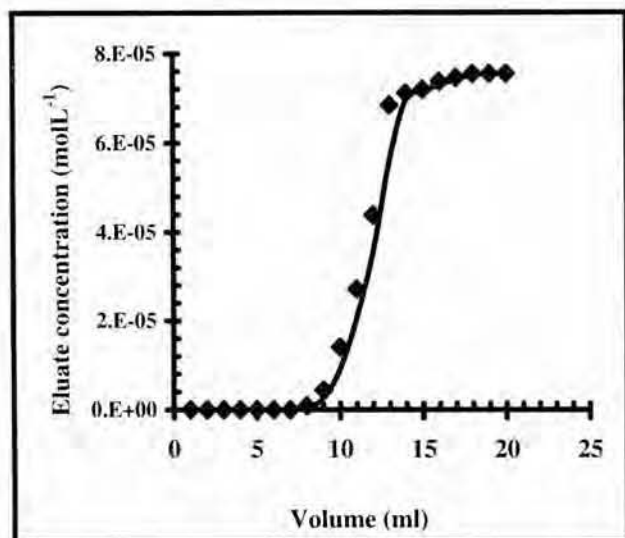


Fig. 3 — Break through curve for the sorption of In (III) ions on modified XAD-16 resin.

Quantitative collection of In(III) ions was possible from solutions of concentration in the order of 5 ppb with recovery up to 99%. Preconcentration factor was found to be 666.

Breakthrough studies—In sorption studies, the breakthrough is depicted when the effluent concentration of any chemical species from the column is about 3-5% of the influent concentration. The breakthrough volume for In(III) ions was observed and noted on x-axis of the plot at the initial rise of the curves. Similarly the total saturation volume (where $C_e \approx C_i$) was observed and noted on x-axis (top) of the plot at the final shape of the curves. The total sorption capacity in $\mu\text{mol g}^{-1}$ was calculated on the basis of total saturation volumes and was found 157.89 ± 2.0 . The sharp profile of the curve (Fig. 3) shows the favourable nature of equilibrium²². It was also observed that initially, the effluent pH decreased significantly then increased and approached to the influent pH value.

Resin stability — The resin stability was checked by subjecting the resin to several loading and elution experiments. The capacity of resin was found to be practically constant (variation of 1-2%) after its repeated use for more than 10 times. Thus, the multiple use of resin column is feasible.

Interferences

Because common ions influence the sorption of metal ions in aqueous solutions, the effect of bicarbonate, bromide, calcium, carbonate, chloride, cobalt, copper(II), iodide, iron(II), iron(III), lithium,

Table 2 — Determination of indium in some environmental water samples

Sample	Indium, $\mu\text{g mL}^{-1}$			
	Added	Found ^a	Recovery % $\pm$ s	RSD %
Tap water	0.0	0.92	± 0.01	1.08
	1.0	1.9	98.9 ± 0.04	2.1
Drinking water	0.0	0.0	± 0.05	
	1.0	2.0	100 ± 0.07	3.5
Industrial water	0.0	1.85	± 0.06	3.2
	1.0	2.83	99.3 ± 0.05	1.7
Ground water	0.0	1.50	± 0.05	3.6
	1.0	2.48	99.2 ± 0.05	2.0

^aAverage of two determinations

lead(II), magnesium, nickel, phosphate, potassium, sodium, sulphate, sulphide and tartrate was examined on the sorption of In(III) ions (1:100 and 1:10 for anions and cations, respectively) onto the synthesized resin. It was observed that only Pb(II) ions reduce the sorption in the range of ~18%. This decrease in the sorption in the presence of lead may be due the replacement of metal ions by lead itself. The complexes of Pb(II) ions with phthalic acid are reported in the literature²³.

Applications of the method

The proposed method was applied to the determination of indium in some environmental water samples. Water samples were filtered to remove the suspended particles. The estimation of metal ion was made with and without standard addition by passing 500 mL of sample through the column packed with 0.5 g of resin and determining the metal by FAAS after elution as described in the procedure. The results are given in Table 2 and show the suitability of the present resin.

Conclusions

It can be concluded from the results that phthalic acid modified Amberlite XAD-16 is an effective sorbent for trace amounts of In(III) ions that can be used for their preconcentration or removal from its dilute aqueous solutions. Under optimal conditions, almost quantitative sorption is achieved on functionalized resin and the metal ions can be desorbed with common mineral acids. These studies show that the synthesized resin has a faster rate of equilibration with high sorption capacity. The sorption data are followed quantitatively by three isotherms namely Langmuir, Freundlich and Dubinin Radushkevich (D-R). The positive value of ΔH and

negative value of ΔG indicate the endothermic and spontaneous nature of the sorption for indium (III) ions. The synthesized resin has minimum matrix interference with common anions and cations studied.

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