

# Preparation and Adsorption Performance of a Novel Chelating Resin Containing Pyrogallol Red

Anuradha Singh<sup>1</sup>, C L Gehlot<sup>2</sup> and D. K. Singh<sup>3\*</sup>

<sup>1</sup>Research & Development Centre, Ranbaxy Laboratories Limited Sarhau, Sector 18, Gurgaon-122015 (Haryana), India

<sup>2</sup>School of Chemical Sciences, Central University of Gujarat, Gandhinagar

<sup>3</sup>Shanti Institute of Technology Kurali, Baghpat Road, Meerut-250501

## Abstract

A novel chelating resin was prepared from polystyrene-divenylbenzene(PS-DVB) beads by coupling it, through the -N=N- group, with pyrogallol red (PGR). The PS-DVB-PGR resin was characterized by infrared spectroscopy and elemental analysis. Adsorption behavior of the resin for Zn<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup> and Au<sup>3+</sup> was investigated by batch experiments. The distribution coefficients (K<sub>d</sub>) of the chelating resin for ten metal ions as a function of pH were determined. The selective uptake of metal ions onto the chelating resin is Pb<sup>2+</sup>>Ag<sup>+</sup>> Fe<sup>3+</sup>> Mn<sup>2+</sup>>Cd<sup>2+</sup>>Zn<sup>2+</sup>>Au<sup>3+</sup>>Cu<sup>2+</sup>>Ni<sup>2+</sup>>Co<sup>2+</sup>. The results indicated that the removal of Pb<sup>2+</sup> was more than 99.5% at pH 5.0. The adsorption capacity of PS-DVB-PGR towards Pb<sup>2+</sup> was found to be 409.6 mg/g. When packed in a column, the new resin is able to separate Ag<sup>+</sup> from Au<sup>3+</sup> and Co<sup>2+</sup>, and Pb<sup>2+</sup> from Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Mn<sup>2+</sup>. Five replicate determinations of 0.386-0.460 mg of metal ions present in 100 mL solution gave recoveries with % error -1.45 - +1.66. The developed method was successfully used for speciation of lead (II) in aqueous samples with 98.0-105.0% recovery.

**Keywords:** PS-DVB-PGR chelating resin; metal ions; separation / removal.

## 1. Introduction

Environmentalists are primarily concerned with the presence of heavy metals due to their toxicity and impact on human health and environment. Lead is highly toxic to human beings. It interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys and reproductive and nervous systems. The presence of high levels of lead in the environment may cause long term health risks to humans and ecosystems. The major sources containing lead are the wastewater from process industries engaged in lead acid battery, paints, oils, metal fossil fuel, forest fibers, mining activity, automobile emission, sewage wastewater, sea spray etc. are just few examples<sup>1-4</sup>.

Chelating resins are of immense value for the separation and removal of toxic metals from the aqueous solutions due to their selectivity and good preconcentration factor<sup>5,6</sup>. S. Tokalioglu and S. Kartal have studied preconcentration of iron(III), lead(II), cobalt(II) and chromium(III) on Amberlite XAD-1180 resin loaded with 4-(2-pyridylazo)-resorcinol and their determination by FAAS<sup>7</sup>. M. Soylak et al.<sup>8</sup> have studied solid phase extraction of iron and lead in environmental matrices on Amberlite XAD-1180/PV. S. Meesri et al. have studied extraction and preconcentration of toxic metal ions from aqueous solution using benzothiazole-based chelating resins<sup>9</sup>. Tokalioglu et al. have synthesized a novel chelating resin and used for selective separation and preconcentration of some trace metals in water samples<sup>10</sup>. A. A. Ensafi et al. have investigated an online preconcentration system for lead(II) determination in wastewater by atomic absorption spectrometry using active carbon loaded with pyrogallol red<sup>11</sup>.

In view of the good complexing properties of pyrogallol red (PGR), it was thought worth to couple this ligand with polystyrene-divinyl benzene (PS-DVB) beads through an -N=N- spacer. This paper describes the preparation of a new chelating resin (PS-DVB - PGR), characterization and analytical applications for separation of metal ions and solid phase extraction of Pb<sup>2+</sup>.

## 2. Experimental Procedure

### Reagents

Styrene and divinylbenzene (Aldrich, USA) and pyrogallol red (Fluka, Switzerland) were used. Stock solutions of Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup> and Au<sup>3+</sup> (0.1 M each) were prepared in demineralized water (DMW) and acidified with the corresponding acid up to pH ~2. The pH (2-6) was adjusted with the buffer solutions (CH<sub>3</sub>COOH or HCl, 0.1 M - CH<sub>3</sub>COONa, 0.1 M). All other reagents used were of analytical grade. The metal ions were analyzed by complexometric titration with EDTA<sup>12</sup> except Ag<sup>+</sup>, Au<sup>2+</sup> and Pb<sup>2+</sup> which were analyzed spectrophotometrically using 2-(2-quinolazo)-5-diethylaminoanil<sup>13</sup>, tin(II) chloride<sup>14</sup> and PAR (2,4-pyridylazoresorcinol)<sup>15</sup>, respectively.

### 3. Apparatus

Temperature controlled rotary shaking machine (IEC-56), Systronics digital pH meter, magnetic stirrer with hot plate, vacuum oven, Euro EA 3000 Series Elemental Analyzer, Shimadzu 8201 PC FTIR spectrophotometer and Systronics UV-VIS double beam spectrophotometer 2203 were used for shaking, pH measurements, stirring, drying, elemental analysis, FTIR studies and spectrophotometric measurements, respectively. Universal V3.9A TA instrument was used for thermogravimetric analysis.

### 4. Preparation of macroporous resin

Polystyrene-divenylbenzene (PS-DVB) copolymer resin was prepared using suspension polymerization process<sup>16</sup>. In this preparation organic phase is prepared by mixing styrene (28 g, 0.304 mol), divinyl benzene (8 g, 0.062 mol), azobisisobutyronitrile (0.4 g, 0.002 mol) and toluene (20 g, 0.2 mol). This organic phase was suspended in an aqueous solution containing distilled water (90 mL), sodium sulphate (4.8 g, 0.003 mol), calcium carbonate (0.8 g, 0.008 mol), and gelatin (0.0028 g). The suspension polymerization process was carried under controlled stirring at  $60 \pm 2^\circ\text{C}$  for 4 h. Then, temperature of the reaction mixture was increased to  $90 \pm 2^\circ\text{C}$  in half an hour, and then it was kept constant for the next 2 h. The resin particles were separated and washed with DMW to remove the excess of calcium carbonate, 0.1 N HCl solution was added to the resin. Again, the resin was washed with DMW and finally with methanol, and then dried in a vacuum oven at  $60-65^\circ\text{C}$ .

### 5. Preparation of chelating resin

The polystyrene-divenylbenzene beads (10 g, 100-150 mesh) were swollen in chloroform and separated by suction. The resin was then treated with 20 mL of conc.  $\text{HNO}_3$  and 50 mL of conc.  $\text{H}_2\text{SO}_4$  and the mixture was stirred at  $60^\circ\text{C}$  for 1 h. Thereafter, the reaction mixture was poured into an ice-water mixture and labeled as PS-DVB- $\text{NO}_2$ . The nitrated resin was filtered, rinsed with DMW until free from acid and then refluxed with a reducing mixture containing 40 g of  $\text{SnCl}_2$ , 45 mL of conc. HCl and 50 mL of  $\text{C}_2\text{H}_5\text{OH}$  at  $90^\circ\text{C}$  for 12 h. After cooling to ambient temperature, the reduction product was filtered off, washed with a mixture of conc. HCl and methanol (1 : 1 V/V), 2 M NaOH and DMW, and labeled as PS-DVB- $\text{NH}_2$ . Then, aminated resin was added to 1 M HCl and diazotized by slow addition of 1 M  $\text{NaNO}_2$  at  $0-3^\circ\text{C}$  until the reaction mixture began to give permanent blue colour with starch-iodide. After the completion of diazotization, the resin was rapidly filtered off, washed with an ice-cold 1% NaCl to pH  $\sim 4$  and reacted at  $4-5^\circ\text{C}$  with pyrogallol red (10 g dissolved in 400 mL of DMW and 200 mL of glacial acetic acid) for 24 h. The blackcoloured beads were filtered, washed with 4 M HCl and DMW and dried at  $50^\circ\text{C}$  over  $\text{P}_2\text{O}_5$  in a vacuum oven. Finally, the chelating resin was labeled as PS-DVB-PGR.

#### FTIR analysis

FTIR analysis was performed by KBr technique.

#### Elemental analysis

The chelating resin was analyzed for carbon, nitrogen and sulfur.

#### Chemical stability

A quantity PS-DVB-PGR resin (0.1 g) was shaken with 0.1-4 M  $\text{HNO}_3$  or alkaline solutions pH 8-11 in a 100 mL stopper Pyrex conical flask for 6 h, filtered off and washed with distilled water until neutral. After drying, the sorption capacity for  $\text{Pb}^{2+}$  was measured by batch adsorption experiment.

#### Batch adsorption experiments

The effect of agitation time with  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  was studied by agitating 25 mL of metal ion solution ( $4 \times 10^{-3}$  M, pH $\sim 5$ ) with 50 mg of chelating resin (100-150 mesh) for 4 h in 100 mL of Pyrex conical flasks at  $25^\circ\text{C}$ . At the end of predetermined time intervals the resin was separated by centrifugation and the remaining metal ions in solution were analyzed. The effect of adsorbent dose on  $\text{Pb}^{2+}$  removal was studied by agitating 50 mL of 50 mg/L solution of  $\text{Pb}^{2+}$  containing different doses of chelating resin for a period of 4 h. The relative adsorption affinities of the chelating resin for ten metal ions at different pH were studied by agitating 50 mg of chelating resin beads with 25 mL of metal ion solutions ( $4 \times 10^{-3}$  M, pH 2-7) for 4 h. After equilibrium, metal ions remaining in the solution were analyzed. The distribution coefficients ( $K_d$ ) were calculated from the following equation:

$$K_d \text{ (mL/g)} = \frac{\text{Amounts of metal ions in resin phase/g}}{\text{Amount of metal ion in solution phase/mL}}$$

### Column separations

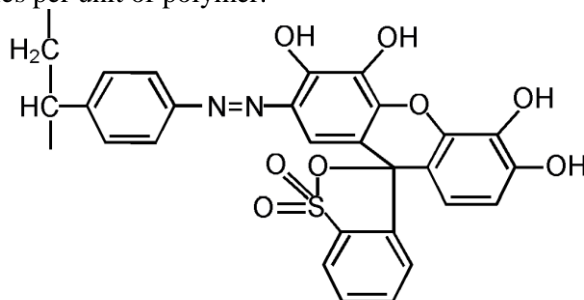
Quantitative separations of analytical importance were achieved on the column of PS-DVB-PGR. One gram of the chelating resin was packed in to a glass column of i.d. 3.9 mm. The column was first washed with about 20 mL of DMW and then the mixture of metal ions having concentration 0.386-0.460 mg/ 10 mL was introduced in to the column and allowed to be adsorbed. The metal ions were then eluted separately using suitable eluting reagents and analyzed. The flow rate was maintained ~0.2 mL/min throughout the elution process.

### Desorption studies

After adsorption experiments, a 50 mg/L solution of  $Pb^{2+}$ -laden chelating resin was separated out by filtration and the filtrate was discarded. The resin was given a gentle wash with DMW to remove any unadsorbed  $Pb^{2+}$ . Desorption studies were carried out using those chelating resin samples agitated with 40 mL of  $HNO_3$  of various strengths (0.1-2.0 M)

## 6. Results and discussion

Pyrogallol Red is a ligand that is widely used for analytical determinations<sup>17-19</sup>. In addition, this ligand acts as a selective complexing agent for  $Pb^{2+}$  at pH = 5 - 6.5. The results of elemental analysis agree well with the assumption that on an average one PGR molecule is present in the chelating resin per unit of polymer as shown in Scheme 1, with two water molecules (per unit of polymer). TGA of the resin studied up to 120°C showed a weight loss ~6.3% which supports the presence of two water molecules per unit of polymer.



Scheme 1- One PGR molecule per unit of polymer

### Characteristics of PS-DVB-PGR chelating resin

FTIR spectra of the intermediates, chelating resin (PS-DVB-PGR) and PGR recorded in KBr matrices are shown in Figs.1 a and b. PS-DVB- $NO_2$  exhibits two strong bands at 1530 and 1347  $cm^{-1}$  which are characteristic of nitro groups. However, these bands disappeared in the infrared spectrum of PS-DVB- $NH_2$  and a strong band due to amine group has been appeared at 1624  $cm^{-1}$  (Fig. 1 a). This shows that PS-DVB- $NH_2$  has been synthesized through reduction of PS-DVB- $NO_2$ . In the spectrum of PS-DVB-PGR, the absorption band at 1531 and 1384  $cm^{-1}$  due to -N=N-, and C-OH groups of PGR molecule are observed and matching several absorption bands at 1589, 1308, 1133, 1011, 772 and 588  $cm^{-1}$  were found in the infra red spectra of PS-DVB-PGR and the PGR monomer (Fig. 1 b) that can be ascribed to PGR functional groups.

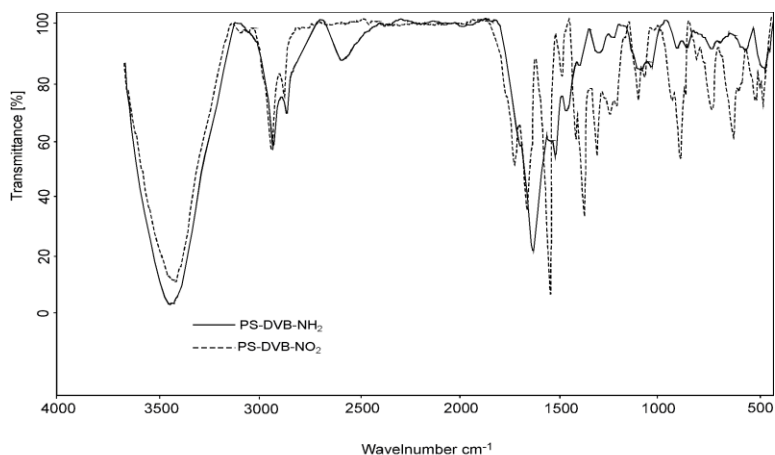


Fig. 1a- FTIR spectra of PS-DVB- $NH_2$  and PS-DVB- $NO_2$  resins.

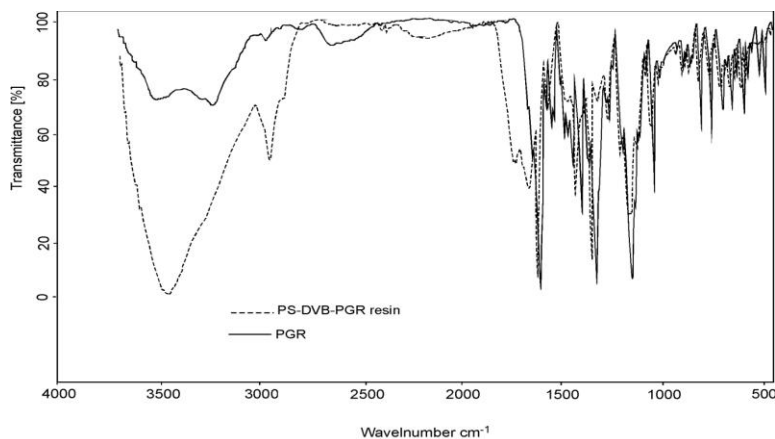


Fig. 1b- FTIR spectra of PS-DVB-PGR resin and PGR

The data of elemental analysis of the chelating resin are as follows:

C, 56.9 % (calculated 57.0 %); H, 3.6 % (calculated 3.5 %); N, 5.0 % (calculated 4.9 %) and S, 5.7 % (calculated 5.6 %).

On the basis of elemental analysis, water content determination (6.3 %) and FTIR data, the following formula of the chelating ligand has been assigned tentatively;  $C_{27}H_{20}N_2O_8S \cdot 2H_2O$

#### Chemical Stability

When the chelating resin was contacted with an acidic solution stronger than 3M  $HNO_3$  or with alkaline solutions above pH 12, the solution became pale yellow (in acidic solutions) or light brown (in alkaline solution). However, decomposition was negligible and no significant difference in sorption capacity for  $Pb^{2+}$  was observed. Hence, the resin is believed to be sufficiently stable in acidic and basic solutions both.

#### Effect of Agitation time

Increased agitation time resulted higher uptake of metal ions and attained equilibrium in 30 min. Approximately 90% of metal ions removed within 10 min. The % removal was found to be ~99.5%.

#### Effect of chelating resin concentration on metal ion adsorption

The effect of adsorbent dosage on the per cent removal of  $Pb^{2+}$  at initial  $Pb^{2+}$  concentration 50 mg/L is shown in Fig. 2. The experimental results revealed that  $Pb^{2+}$  removal efficiency increases up to the optimum dosage. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial  $Pb^{2+}$  concentration, because for a fixed initial solute concentration, increasing adsorbent dose provides a larger surface area or more adsorption sites. It is evident that for a quantitative removal of 50 mg/L of  $Pb^{2+}$  in 50 mL, minimum chelating resin content of 50 mg is required for ~ 99% removal.

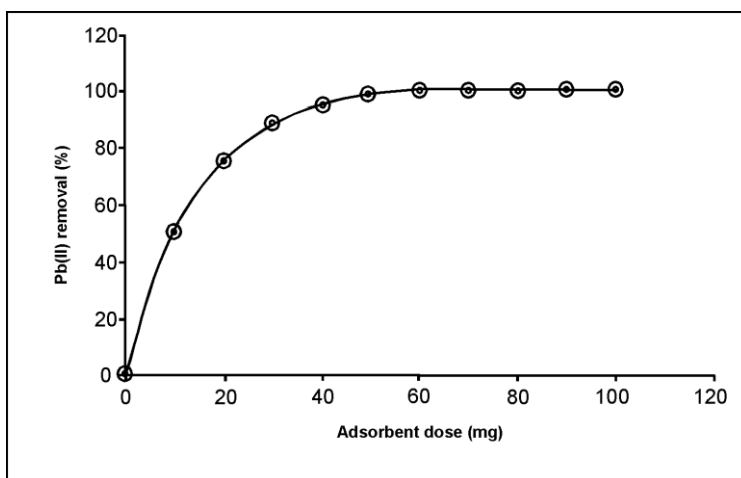


Fig. 2-Effect of chelating resin dosage on  $Pb^{2+}$  removal conditions: [ $Pb^{2+}$  50  $mL^{-1}$ ; pH~5; contact time 4 h]

#### Effect of initial pH

Table 1 presents the effect of initial pH on the distribution coefficients of 8 heavy metal ions;  $Ag^+$  and  $Au^{3+}$ . The  $K_d$  values decreased with decreased initial pH of metal ion solution. This is due to the fact that in acidic solution, the

formation constant of metal ion-PGR decreases due to protonation of PGR, whereas at higher pH (>6), metal ions react with hydroxyl ions to produce their hydroxides. The chelating resin shows greatest selectivity (highest  $K_d$ ) for  $Pb^{2+}$  due to large  $Pb^{2+}$ -PGR formation constant.

**Table 1-** Distribution coefficients of metal ions on PS-DVB-PGR resin (n = 3)

Metal ions	pH 2	pH 4	pH 6	Distilled water (pH ~ 7)
Zn <sup>2+</sup>	16	38	65	69
Cd <sup>2+</sup>	18	41	68	70
Mn <sup>2+</sup>	20	62	79	80
Cu <sup>2+</sup>	22	45	52	55
Ni <sup>2+</sup>	10	24	33	34
Co <sup>2+</sup>	8	23	30	30
Fe <sup>3+</sup>	31	68	84	88
Pb <sup>2+</sup>	678	2121	3063	3075
Ag <sup>+</sup>	126	220	265	266
Au <sup>3+</sup>	24	51	58	59

### Separations

The quantitative separations of metal ions having  $K_{dA} / K_{dB} \geq 4.5$  were tried on a mini column of the chelating resin. Those achieved experimentally are summarized in Table 2.

**Table 2-** Quantitative separations of metal ions achieved on the column of ST-DBV-PGR resin

Sl. No.	Metal ion	Eluents	Volume of effluent (mL)	Metal ion loaded ( $\mu$ g)	Metal ion recovered (n = 3) ( $\mu$ g)	% Error
1	Au <sup>3+</sup>	A	30	195	196	+0.51
	Ag <sup>+</sup>	B	40	212	210	-0.94
2	Cu <sup>2+</sup>	A	30	248	250	+0.80
	Ag <sup>+</sup>	B	40	212	210	-0.94
3	Co <sup>2+</sup>	A	30	234	234	0.00
	Ag <sup>+</sup>	B	40	212	209	-1.41
4	Ni <sup>2+</sup>	A	30	180	183	+1.66
	Pb <sup>2+</sup>	C	40	206	203	-1.45
5	Cu <sup>2+</sup>	A	30	248	251	+1.21
	Pb <sup>2+</sup>	C	40	206	204	-0.97
	Mn <sup>2+</sup>	A	30	215	6	+0.93
	Pb <sup>2+</sup>	C	40	206		-0.97
	Cd <sup>2+</sup>	A	30	224		+0.45
	Pb <sup>2+</sup>	C	40	206	7	-1.45

A = 0.01 M HNO<sub>3</sub>, B = 0.5 M HNO<sub>3</sub>, C = 1 M HNO<sub>3</sub>

### Desorption studies

Desorption studies help to elucidate the adsorption mechanism. The desorption process allowed the recovery of precious metals from wastewater and regeneration of the adsorbent. The effect of HNO<sub>3</sub> concentration on the desorption of Pb<sup>2+</sup> was studied. The maximum desorption of Pb<sup>2+</sup> was about 99 % with 1 M HNO<sub>3</sub>.

### 7. Applications

The developed method has been applied for the preconcentration and recovery of Pb<sup>2+</sup> in water samples. For each sample, 1000 mL was passed through the column at the rate of ~3 mL/min. Then, the Pb<sup>2+</sup> contents in the washed solution were estimated by FAAS. The results listed in Table 3 indicate the suitability of the present chelating resin for preconcentration and recovery of Pb<sup>2+</sup> from natural water samples.

**Table 3-** Determination of Pb<sup>2+</sup> in water samples (pH ~ 6, n = 5)

Sample	Pb <sup>2+</sup> added (µg/mL)	Pb <sup>2+</sup> found (µg/mL)	Recovery, %
Distilled water	-	0.0	-
	10	9.8 ± 0.3	98
	50	51.7 ± 0.5	103.4
	100	103.2 ± 0.6	103.2
Tap water	-	0.0	-
	10	10.1 ± 0.4	101
	50	52.2 ± 0.5	104.4
	100	104.3 ± 0.6	104.3
Sea water	-	0.0	-
	10	9.9 ± 0.4	99.0
	50	52.6 ± 0.6	105.2
	100	103.8 ± 0.6	103.8
Wastewater	-	11.3 ± 0.5	-
	10	21.6 ± 0.5	103.0
	50	63.8 ± 0.6	105.0

## 8. Conclusions

Chelating resins find broad applications as preconcentration and separations matrixes for metal ions. The proposed method provides a simple, selective, fairly rapid and reliable technique for separation of some metal ions of analytical interest and removal of lead from the environmental samples. The matrix effects with the method are reasonably tolerable. The elution was easily performed with 1 M HNO<sub>3</sub>. The chelating resin is stable for several treatments of the sample solutions, without the need to use any chemical reagents. The chelating resin can be easily regenerated through 1 M HNO<sub>3</sub> washing and the adsorption capacity retained more than 97% after 5 cycles, showing a promising application for the treatment of liquid environment samples. The recovery of spliced Pb<sup>2+</sup> was in the range of 98-102%.

\*\* This work is a part of Ph. D. thesis of Anuradha Singh carried out at Harcourt Butler Technological Institute, Kanpur.

## References

- Jalali R, Ghafourian H, Asef Y, Davarpanah S J & Sepehr S, *J Hazard Mater B*, 92 (2002) 253.
- Gupta V K, Gupta M & Sharma S, *Water Res*, 35 (2001) 1125.
- Conrad K & Hansen H C B, *Bioresour Technol*, 98 (2007) 89.
- Colby G R & Kimberly L O, *Environ Sci Technol*, 32 (1998) 987.
- Pramanik S, Dhara, P K & Chattopadhyay P, *Talanta*, 63 (2004) 485.
- Costa L C, Gomes A S, Coutinho F M B & Teixeira, V G *React Funct Polym*, 70 (2010) 738.
- Tokalioglu S, Buyukbas H & Kartal S. *J Braz Chem Soc*, 17 (2006) 98.
- Soylak M, Tuzen M & Narin I, *Quim Nova*, 29 (2006) 203.
- Meesri S, Praphairaksit N, Imyim A, *Microchem J*, 87 (2007) 47.
- Tokalioglu S, Yilmaz V, Kartal S, Delibas A & Soykan C, *J Hazard Mater*, 169 (2009) 593.
- Ensafi A A, Khayamian T & Karbasi M H, *Anal Sci* 19 (2003) 953.
- Vogel A, *A text book of quantitative inorganic analysis* (ELBS and Longmans, London), 1962.
- Hu Q, Guangyu Y, Huang Z & Yin J, *Talanta* 58 (2002) 467.
- Sandell E B, *Colorimetric determination of traces of metals* (Inc. N.4, Interscience Publisher), 1959.
- Ferreira S L C, Andrade M G M, Lobo, I P & Costa, A C S, *Anal Lett*, 24 (1991) 1675.
- Jayaswal N, Sinha, S & Kumar A, *J Appl Polym Sci*, 79 (2001) 1735.
- Ensafi A A & Chamjangali M A, *Spectrochim Acta Part A*, 58 (2002) 2835.
- Ensafi A A & Keyvanfard M, *Spectrochim Acta Part A*, 58 (2002) 1567.
- Ensafi A A, Rezaei B & Beglari, M, *Anal Lett*, 35 (2002) 909.