

Separation of iron and cobalt using ^{59}Fe and ^{60}Co by dialysis of polyvinylpyrrolidone–metal complexes: A greener approach

Susanta Lahiri^{a,*}, Soumi Sarkar^b

^aChemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India

^bDepartment of Biomedical Sciences, Bundelkhand University, Jhansi 284128, India

Received 31 July 2006; received in revised form 3 October 2006; accepted 15 November 2006

Abstract

An environmentally benign method to separate iron and cobalt has been developed using a safe chemical, polyvinylpyrrolidone (PVP). The method involves dialysis of PVP–Fe and PVP–Co complexes against triple-distilled water. ^{59}Fe and ^{60}Co were used as radioactive tracers of iron and cobalt throughout the experiment. No other chemicals are required for clean separation of cobalt from iron. The optimum condition for separation has been obtained at pH 5 using 10% aqueous solution of PVP. The method is applicable from trace scale to macro-scale. Very high separation factors have been obtained.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Dialysis; Polyvinylpyrrolidone; Fe–Co separation; ^{59}Fe ; ^{60}Co

1. Introduction

Usage of toxic chemicals for several generations has been a major cause of deterioration of the state of our surroundings; the very existence of mankind is now at stake. Keeping in mind the gravity of the problem, officials are encouraging greener versions of chemistry. The major agenda of green chemistry are to design chemical products and processes that can reduce or eliminate the use and generation of hazardous substances. Usage of chemicals having less toxicity is one route that can save the earth.

Polyvinylpyrrolidone (PVP) is a synthetic homopolymer, readily prepared from its monomer *N*-vinyl-2-pyrrolidone. Thanks to its excellent biocompatibility and chemical inertness, it has been extensively applied in drug formulation and other clinical and biological fields. The polymer has a wide range of solubility in a large number of organic solvents; but the unique property of the polymer that can be utilized in green chemistry process is that the polymer is soluble in water.

The chemical structure of PVP suggests that its complex formation ability is at acidic pH; and the same has been demonstrated by the formation of Co–PVP and I–PVP complexes (Li et al., 1990; Schenck et al., 1979). PVP has been already used as an extracting agent for metal cations like Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Hg(II), Cr(III), and Fe(III) (Maturana et al., 2000). They made PVP soluble in *n*-octanol, *n*-decanol, and *n*-dodecanol with benzene and kerosene as modifiers and extracted the cations from HCl/HNO₃ solution onto the organic phase consisting of PVP–kerosene/*n*-dodecanol–benzene using liquid–liquid extraction technique. The work of Maturana et al. (2000) can be designated as the first systematic study on the metal ions binding ability of PVP, but at the same time their work is the opposite of a greener approach because they have used carcinogenic organic solvents like kerosene and benzene as organic phases. The chemistry of the polymer PVP has been studied by Tokman et al. (2004). They preconcentrated Pb, Cu and Mn by the water-soluble polymer PVP using a precipitation technique. They concluded that PVP forms complexes with metals via oxygen and nitrogen, due to the high polarity of the lactam ring conferred by resonance stabilization facilitated by a near-planer ring geometry. Apart from these, metal

*Corresponding author.

E-mail address: susanta.lahiri@saha.ac.in (S. Lahiri).

complexations (Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Fe(III), and Cr(III)) with some cross linked PVP like poly(4-vinylpyrrolidone)-g-poly(*N*-hydroxyacrylamide), poly(acrylamide-co-1-vinyl-2-pyrrolidone) and poly(*N,N'*-dimethyl acrylamide-co-1-vinyl-2-pyrrolidone) have also been studied (Pande et al., 2000; Rivas et al., 1999).

Earlier, several methods were employed for separation/extraction of iron and cobalt. A large number of works have been carried out using liquid–liquid extraction or chromatographic techniques. Various reagents and stationary phases in the chromatographic column like Cynex 272 (Ghandhi et al., 1993), 2-pyridinecarboxaldehyde phenylhydrazone (Watanesk and Schilt, 1986), 2-thiophenylaldehyde-4-phenyl-3-thiosemicarbazone (Khuhawar and Lanjwani, 1998), Chromosorb 108 (Tuzen et al., 2005), Diaion HP-2MG, Dithizone chelates (Tuzen and Soylak, 2004), etc., were used for the purpose. Liquid–liquid extraction and separation of iron(III) with 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester was carried out by Jayachandran and Dhadke (1997). Cloud point extraction of iron(III) and vanadium(V) was carried out using 8-quinolinol derivatives and Triton X-100 (Ohashi et al., 2005).

All the methods described above either require a lot of organic solvents for dilution of the reagents or use insoluble polymers as the stationary phase. For cleaner chemistry, it is always better to avoid carcinogenic organic reagents. However, no attempt has yet been made for separation of Fe and Co using PVP. Liu et al. (2000) investigated the formation of Fe³⁺–PVP and Co²⁺–PVP complexes and reported their coordination stability constants as 10 and 0.6, respectively. Therefore we predict that PVP may selectively bind with Fe in the presence of Co and that the separation between the pairs may be possible. PVP, having an added advantage of being water soluble, can be used for extraction and separation without the necessity of organic solvents.

In this paper, separation of cobalt and iron in both trace and macro-scale has been reported by exploiting the complex formation property of PVP and by dialyzing the mixture of Fe–/Co–PVP complexes against triple distilled water. ⁵⁹Fe (*T*_{1/2} = 44.5 d) and ⁶⁰Co (*T*_{1/2} = 5.27 y) were used as radiotracers of iron and cobalt, respectively.

2. Materials and methods

PVP solutions of different strengths (1%, 5%, 10% and 20%) were prepared by dissolving required amounts of the polymer in triple distilled water. ⁵⁹Fe was procured from the Board of Radiation and Isotope Technology, India. The radioactive iron solution was an old stock (used after ~2.5 half lives) and the impurity of ⁶⁰Co was found in the ⁵⁹Fe solution itself. Therefore there was no need of adding ⁶⁰Co separately. Besides the trace amount of iron and cobalt solution, macro-amounts of FeCl₃ as well as CoCl₂ solution of different strengths were prepared and the radioactive solution was properly spiked to form the

mixture of macro-quantities of iron(III) and cobalt(II) in solution. Dialysis sacs (D6066-25EA), procured from SIGMA-ALDRICH, were cut into suitable lengths according to the various volumes of dialysis solutions. Dialysis was carried out on a magnetic stirrer. Iron and cobalt was monitored by measuring the area of characteristic photo peaks: 1098.6 keV (⁵⁹Fe) and 1173.2 keV (⁶⁰Co), respectively. The mixtures of iron and cobalt salts either in trace or macro-scale were dialyzed against triple distilled water. After a definite time interval, the counts of ⁵⁹Fe and ⁶⁰Co in the dialysis sac were taken with the help of an HPGe detector of 2.13 keV resolution in conjunction with a PC-based multichannel analyzer and compared with the initial count of the dialysis sac.

First, the study of complexation of PVP with the metal ions of Fe³⁺ and Co²⁺ was carried out by varying the pH of the solution and keeping PVP concentration fixed. Once the optimum pH for separation was observed, all other experiments were carried out at the optimal pH 5.

3. Results and discussion

3.1. Experiment with trace scale ⁵⁹Fe and ⁶⁰Co

To study the separation of ⁵⁹Fe and ⁶⁰Co in trace scale, first of all we mixed the 5% PVP solution and the mixture of iron and cobalt solutions. This combination was put in the dialysis sac. The pH of the mixture was adjusted according to experimental condition with HCl or NH₃ as per the requirement. Dialysis was carried out against triple distilled water with different pH values of the PVP–Fe/Co mixture to get the optimum condition for dialysis. The separation factor has been calculated using the following formula:

$$SF = \frac{D_{Co}}{D_{Fe}}$$

Here

$$D_{Co} = \frac{\text{Count of } ^{60}\text{Co in dialysate}}{\text{Count of } ^{60}\text{Co in the dialysis sac}}$$

and

$$D_{Fe} = \frac{\text{Count of } ^{59}\text{Fe in dialysate}}{\text{Count of } ^{59}\text{Fe in the dialysis sac}}$$

First, trace amounts of ⁵⁹Fe and ⁶⁰Co incubated with PVP are subject to dialysis. To get an idea about the best pH for separation, we varied the pH of the radionuclides + PVP mixture while keeping the concentration of PVP fixed at 5%. The highest separation factor (~10 000) between cobalt and iron has been obtained at pH 5 after 2 h of dialysis time. During 2 h, ~33% of pure cobalt comes out from dialysis sac without any contamination from iron. However, after 2 h, some amount of ⁵⁹Fe is also leached out of dialysis sac; this reached to ~8% at 4 h, while at that time the amount of ⁶⁰Co increased in the dialysate up to an extent of ~46% (Fig. 1).

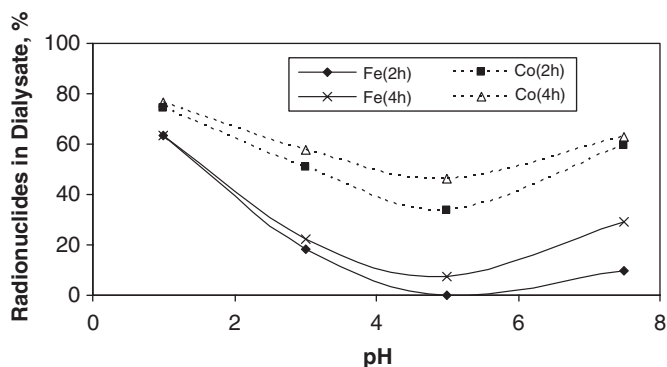


Fig. 1. Dialysis of trace amount of ⁵⁹Fe/⁶⁰Co-PVP mixture at varying pH keeping PVP concentration at 5%.

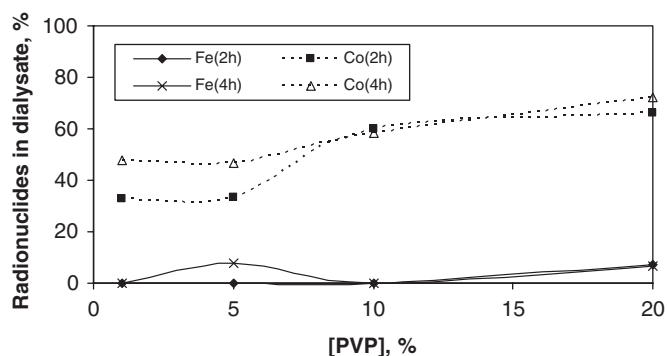


Fig. 2. Dialysis of trace amount of ⁵⁹Fe/⁶⁰Co-PVP mixture at varying PVP concentration keeping pH of the radionuclides + PVP mixture fixed at 5.

To identify the best condition, we varied the concentration of PVP while keeping the pH of the radionuclides + PVP mixture fixed at 5. We found that at 10% PVP concentration and at pH 5, ~60% cobalt is present in the dialysate without any contamination from iron. At this condition, the separation factor of trace amount of cobalt and iron has been found as high as ~25 000. Fig. 2 shows the percentage of iron and cobalt radionuclides in the dialysate after 2 and 4 h of dialysis. Therefore, it is possible to separate trace amounts of pure cobalt from iron only by exploiting the differences in the stability of Fe-PVP and Co-PVP complexes without using any other chemicals. Again the separation is best at nearly neutral pH, i.e. involvement of strong acids, etc. is also nullified in this method.

In order to get an idea about the stability of these complexes, the retention of ⁵⁹Fe or ⁶⁰Co in the dialysis sac has been checked after definite time intervals. Assuming first order reaction between PVP and Fe/Co radionuclides the dissociation rate of PVP-radionuclide complex will be

$$-\frac{d\{(ML)^{m+n}\}}{dt} = k_d \cdot \{(ML)^{m+n}\} - k_a \cdot \{M^m\} \cdot \{L^n\}.$$

Here *M* represents Fe/Co and *L* represents PVP.

The determination of dissociation constant may be evaluated with the help of FISRE (free-ion selective

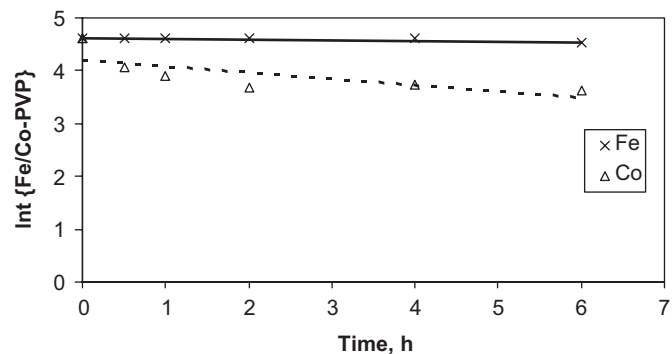


Fig. 3. Dissociation of Fe-PVP and Co-PVP complexes with respect to time when dialyzed against triple distilled water.

radiotracer extraction) technique (Wierczinski et al., 2006; Doornmalen et al., 2000). During dialysis of the PVP-metal complexes, the dissociated metal ions are continuously removed from the dialysis sac. Therefore, it may be assumed that reassociation does not take place. Then the above equation may be simplified as follows:

$$\frac{d\{(ML)^{m+n}\}}{dt} = -k_d \cdot \{(ML)^{m+n}\}.$$

The solution of the differential equation is

$$\{(radioactive\ ML)_t^{m+n}\} = \{(radioactive\ ML)_{t_0}^{m+n}\} \cdot e^{-k_d t}.$$

A plot of time vs. ln{Fe-PVP} or ln{Co-PVP} will give an idea about the dissociation constant (*k_d*) by measuring the slope of the plot.

Log_e{metal-PVP} association in the dialysis sac has been plotted with respect to time in Fig. 3; which shows the *k_d* of Fe-PVP complex is 0.0119 h⁻¹ and the same for Co complex is 0.1177 h⁻¹; i.e. Fe-PVP complex is much more stable than the Co-PVP complex. The dissociation constants determined may, however, slightly differ from their true value as the reassociation between radionuclides and PVP is completely ignored.

3.2. Experiment with macro-amounts of both iron and cobalt

The separation of iron and cobalt was also tried in macro-scale. For this, equal volumes of particular strengths of FeCl₃ (10⁻⁴–10⁻¹ M) and CoCl₂ (10⁻⁴–10⁻¹ M) were mixed together; measured amounts of radioactive solution containing ⁵⁹Fe and ⁶⁰Co were then added to this solution. We wanted to ascertain the same chemical forms so the whole solution was evaporated to dryness and redissolved. The pH of the solution was adjusted to 5 with dil. HCl because the trace scale experiments showed that the optimum pH for the experiment is pH 5.

Fig. 4 shows percentage of iron and cobalt in dialysate after 2 and 4 h of dialysis against the concentration of iron and cobalt (keeping PVP concentration fixed at 10%). It is clear from Fig. 4 that the separation of cobalt from iron is better in macro-scale. The rate of release of cobalt from the

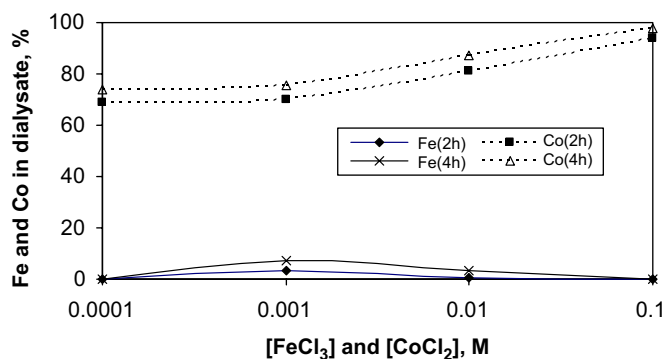


Fig. 4. Percentage of iron and cobalt in dialysate with respect to variation of concentration of Fe/Co when dialyzed with 10% PVP at pH 5.

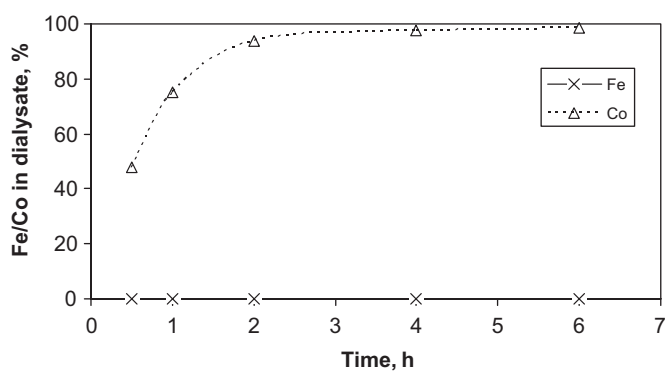


Fig. 5. Dialysis profile of Fe/Co with respect to time when mixture of 0.1 M Fe and 0.1 M Co is dialyzed with 10% PVP at pH 5.

dialysis sac in macro-scale is higher than that of trace scale due to much higher differences in concentration inside and outside the dialysis sac. The result also indicates that Fe forms very strong complexes with PVP. When mixture of 10^{-1} M FeCl_3 and CoCl_2 is dialyzed by equal volumes of 10% PVP solution at pH 5, a separation factor as high as $\sim 5 \times 10^5$ can be achieved after 4 h of dialysis. At this condition, $\sim 98\%$ cobalt comes out from the dialysis sac without any contamination from iron. Fig. 5 shows the dialysis profile of a mixture of 0.1 M FeCl_3 and 0.1 M CoCl_2 with respect to time. In pH 5, Fe^{3+} mainly exists as $[\text{Fe}(\text{III})_3(\text{OH})_4]^{5+}$ (75%) and $[\text{Fe}(\text{III})(\text{OH})_2]^{+}$ ($\sim 21\%$), while cobalt exists as free $\text{Co}(\text{II})^{2+}$ (100%) (Wierczinski et al., 2006; <http://home.tiscali.nl/cheaqs/>); these data also explain the fast dialysis of cobalt from mixture of Fe–Co–PVP solution. Figs. 6a and b are γ -spectra of mixture of 0.1 M FeCl_3 and 0.1 M CoCl_2 (spiked with radioactive solution of ^{59}Fe and ^{60}Co) in the dialysis sac before and after dialysis.

3.3. Experiment with trace amount of cobalt and macro-amount of iron

Experiments were also carried out in the presence of macro-amounts of iron but with only trace amounts of cobalt. This is to simulate situations like a separation of

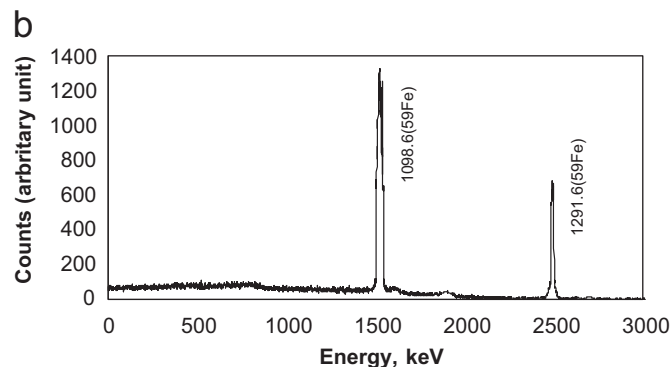
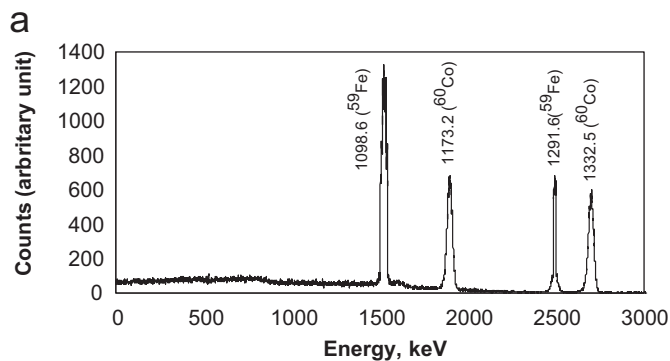


Fig. 6. A γ -spectra of (a) mixture of spiked 0.1 M Fe and 0.1 M Co before dialysis (b) after 4 h of dialysis

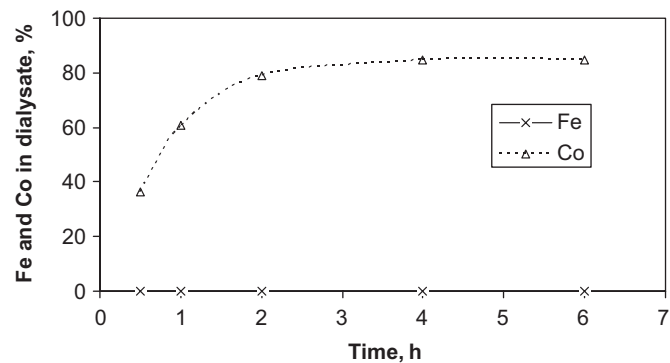


Fig. 7. Dialysis profile of Fe/Co with respect to time when macro-amount of Fe(0.01 M) and trace amount of cobalt is dialyzed with 10% PVP at pH 5.

no-carrier-added ^{57}Co radionuclides produced through $^{56}\text{Fe}(p, n)^{57}\text{Co}$ types of reaction. In such situations, the target matrix is in bulk quantity but the product is in ultra trace scale. We have simulated the situation by repeating the experiment as above but only increasing the amount of iron to 0.01 M. Fig. 7 shows the dialysis profile of trace amount of cobalt and bulk iron. After 4 h we found that about 85% cobalt comes out of the dialysis sac without any contamination, with a separation factor more than 50 000. Therefore clean separation of trace amount of cobalt from bulk iron is possible using the developed methodology.

Wuepper and Povov (1969) reported that a shift of carbonyl band was observed in the IR spectrum of

2-pyrrolidone and the metal cations. The interaction between PVP and metal cations may either be attributed to the donation of a pair of electrons from the carbonyl oxygen to the metal cations, or to the complex formation of the nitrogen on the 5-membered *N*-containing heterocycles with the metal cations. The electron transfer from nitrogen to the metal cations may affect the polarizability of the neighboring oxygen atom (Wuepper and Povov, 1969; Hirai et al., 1985).

4. Conclusion

The separation technique employed for both trace as well as macro-quantity of iron and cobalt in this experiment fulfills the agenda of green chemistry as all the dialysis processes described above used only deionized water. Coupled to this, PVP is one of the most suitable polymers, frequently used as an inert binder of drug. Again, PVP–Fe complexes can be exploited in the field of radioendotherapy where the former can play a dual role in therapy as well as diagnosis.

References

- Doornmalen, J. van, Elteren, J.T. van, Goeij, J.J.M. de, 2000. A chromatographic technique to investigate the lability of copper complexes under steady-state conditions using high specific activity ^{64}Cu . *Anal. Chem.* 72, 3043–3049.
- Ghandhi, M.N., Deorkar, N.V., Khopkar, S.M., 1993. Solvent extraction separation of cobalt(II) from nickel and other metals with cyanex 272. *Talanta* 40, 1535–1539.
- Hirai, H., Chawanya, H., Toshima, N., 1985. *Reac. Polym.* 3, 127.
- Jayachandran, J., Dhadke, P.M., 1997. Liquid–liquid extraction separation of iron (III) with 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester. *Talanta* 44, 1285–1290.
- Khuhawar, M.Y., Lanjwani, S.N., 1998. Liquid chromatographic determination of cobalt(II), copper(II) and iron(II) using 2-thiophen-aldehyde-4-phenyl-3-thiosemicarbazone as derivatizing reagent. *Talanta* 46, 485–490.
- Li, V.A., Zinovev, P.V., Rashidova, S.Sh., 1990. *Uzb. Khim Zh.* 3, 49–50.
- Liu, M., Yan, X., Liu, H., Yu, W., 2000. An investigation of the interaction between polyvinylpyrrolidone and metal cations. *React. Funct. Polym.* 44, 55–64.
- Maturana, H.A., Peric, I.M., Pooley, S.A., Rivas, B.L., 2000. Poly(*N*-vinylpyrrolidone) as metal ion liquid–liquid extractant. *Polym. Bull.* 45, 425–429.
- Ohashi, A., Ito, H., Kanai, C., Imura, H., Ohashi, K., 2005. Cloud point extraction of iron(III) and vanadium(V) using 8-quinolinol derivatives and Triton X-100 and determination of 10^{-7} mol dm $^{-3}$ level iron(III) in riverine water reference by a graphite furnace atomic absorption spectroscopy. *Talanta* 65, 525–530.
- Pande, C.S., Mehta, I.K., Ambasta, B.K., Archana, M., 2000. Preparation of poly(4-vinylpyrrolidone)-*g*-poly(*N*-hydroxyacrylamide) and study of its metal binding properties. *J. Appl. Polym. Sci.* 77, 475–483.
- Rivas, B.L., Pooley, S.A., Soto, M., Geckeler, K.E., 1999. Water-soluble copolymers of 1-vinyl-2-pyrrolidone and acrylamide derivatives: synthesis, characterization, and metal binding capability studied by liquid-phase polymer-based retention technique. *J. Appl. Polym. Sci.* 72, 741–750.
- Schenck, H.U., Simek, P., Haedicke, E., 1979. *J. Pharm. Sci.* 68, 1505.
- Tokman, N., Akman, S., Ozeroglu, C., 2004. Determination of lead, copper and manganese by graphite furnace atomic absorption spectrometry after separation/concentration using a water-soluble polymer. *Talanta* 63, 699.
- Tuzen, M., Soylak, M., 2004. Column system using diaion HP-2MG for determination of some metal ions by flame atomic absorption spectrometry. *Anal. Chim. Acta* 504, 325–334.
- Tuzen, M., Soylak, M., Elci, L., 2005. Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108. *Anal. Chim. Acta* 548, 101–108.
- Watanesk, S., Schilt, A.A., 1986. Separation of some transition–metal ions on silica-immobilized 2-pyridinecarboxaldehyde phenylhydrazone. *Talanta* 33, 895–899.
- Wierczinski, B., Denkova, A.G., Peters, J.A., Wolterbeek, H.T., 2006. Kinetic stability of metal complexes—determination of k_a and k_d using radiotracers. In: Lahiri, S., Nayak, D., Mukhopadhyay, A. (Eds.), *Application of Radiotracers in Chemical, Environmental and Biological Sciences*. Saha Institute of Nuclear Physics, Kolkata, India, p. 112.
- Wuepper, J.L., Povov, A.J., 1969. *J. Am. Chem. Soc.* 91, 4352.