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Talanta 65 (2005) 441–452

Talanta

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Preconcentrative separation of palladium(II) using palladium(II) ion-imprinted polymer particles formed with different quinoline derivatives and evaluation of binding parameters based on adsorption isotherm models

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Received 21 January 2004; received in revised form 21 June 2004; accepted 28 June 2004

Abstract

Palladium(II) ion-imprinted polymer (IIP) materials were synthesized by thermally polymerizing the ternary complexes of palladium(II) with amino (AQ) or hydroxy (HQ) or mercapto (MQ) derivatives of quinoline and 4-vinyl-pyridine. The functional and crosslinking monomers used during polymerization were 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA). 2,2′-Azobisisobutyronitrile (AIBN) and 2-methoxy ethanol were used as the initiator and porogen, respectively. The resulting polymer materials were dried in an oven at 80 °C, ground and sieved to obtain IIP particles which were then subjected to leaching with 50% (v/v) HCl to obtain the leached palladium(II) IIP particles. Control polymer (CP) particles were also prepared by following the above procedure described for IIP particles. The CP particles, unleached and leached AQ-based IIP particles were then characterized by IR, XRD and microanalysis studies. Analytical studies such as preconcentration of palladium(II) from dilute aqueous solutions and separation studies in the presence of selected noble and base metals which co-exist with palladium(II) in its ore or mineral deposits were systematically studied using CP and IIP particles and are compared. AQ-based IIP particles gave higher percent extraction and selectivity coefficients compared to HQ- or MQ-based IIP particles. Five replicate determinations of 25 μg of palladium(II) present in 500 ml of aqueous solution, when subjected to preconcentration and determination by iodide-Rhodamine 6G procedure gave a mean absorbance of 0.104 with a relative standard deviation of 2.25%. The detection limit corresponding to three times the standard deviation of the blank was found to be 5.0 μg of palladium(II) per litre. The rebinding studies using AQ-, HQ- and MQ-based IIPs were carried out and were fitted to the different adsorption isotherm models, viz. Langmuir (L), Freundlich (F) and Langmuir–Freundlich (LF). These adsorption models were used for the evaluation of binding parameters and in elucidating the nature and type of bonding in the IIPs. The results of rebinding experiments showed discrimination between the three IIPs based on the donor atoms of the ligands.

Keywords: Ion imprinting; Palladium(II); Preconcentrative separation; Adsorption isotherms

1. Introduction

Molecular imprinting is a technique for preparing polymeric materials that are capable of high molecular recognition. The resultant imprints possess a steric and chemical memory for the template. Wulff [1] has introduced the concept of covalent molecular imprinting and has developed molecular-imprinted polymers (MIPs) over the years for carbohydrates, amino acids and their derivatives. Haupt and Mosbach [2] developed the non-covalent approach for: (i) the resolution of optical enantiomers and biomolecules; and (ii) the development of sensors and catalysts, etc.

Noble metals especially palladium is very resistant to acids, heat and corrosion and, therefore, used as a precious metal in jewellary and in some forms of chemical apparatus. It is also an excellent conductor of electricity and is

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doi:10.1016/j.talanta.2004.06.024

used for electrical contacts and in catalytic converters [3]. In addition to primary deposits, noble metals occur as very dilute solid solutions in the ores and minerals, with perhaps a few grains of noble metals occurring sparcely throughout [4]. Hence, the recovery of individual noble metals requires a preconcentrative separation from lean aqueous mineral solutions. Vlasankova and Sommer [5] have reviewed various solid phase extraction procedures developed for palladium and other noble metals. Recently, Rao and Sobhi [6] have critically reviewed various preconcentration procedures reported for palladium and platinum since 1990. Ion-imprinted polymers (IIPs) are similar to MIPs but they can recognize metal ions after imprinting and retain all the virtues of MIPs. A particularly promising application of IIP (similar to MIP) is the solid phase extractive preconcentration and or separation from other coexisting ions or complex matrix. Thus, ion-imprinted polymers for solid phase extraction (IIP-SPE) is a fast developing area for the application of IIP technology. Again, Rao et al. [7] in their latest review described the preparation of tailored materials for preconcentration/separation of metals by ion-imprinted polymers for solid phase extraction.

The invention by John et al. [8] relates to the detection and extraction of uranyl ions by polymer imprinting wherein the complexible functionality has the formula CTCOOH, where T is a hydrogen or any halogen (preferably chlorine) methyl and halogen substituted forms thereof CCOOH or PhCOOH. Dai et al. [9] prepared mesoporous sorbent materials with the ion imprinting technique for the separation of aqueous solutions using bifunctional ligands, such as amines, sulphonic acids and phosphonic acids. Gladis and Rao [10] have patented a process consisting of synthesis of SPE materials by polymer imprinting suitable for uptake of uranyl ions from aqueous and synthetic sea water solutions and also in presence of a host +2, +3 and +4 metal ions. Recently Kala et al. [11] have patented the synthesis of ion-imprinted polymer particles for solid phase extractive preconcentration of erbium ion. To our knowledge, there are no patents on IIP-SPE of palladium. Sobhi et al. [12] have prepared IIP materials with nanopores after isolation of palladium (II)–dimethyl glyoxime–4-vinyl pyridine ternary complex and copolymerizing with styrene and divinyl benzene (95%) in presence of 2,2′-azobisisobutyronitrile (AIBN) as initiator.

The main aim of the present work is to compare the percent enrichment of palladium(II) and separation of palladium(II) from selected inorganics using different quinoline derivatives, viz. 8-aminoquinoline (AQ), 8-hydroxyquinoline (HQ) and 8-mercaptoquinoline (MQ) as one of the ligands during the synthesis of IIPs employing ternary mixed ligand complex with palladium(II) in presence of 4-vinyl pyridine. The polymerization was carried out by solubilizing ternary complexes in 2-methoxy ethanol (porogen) and using hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) as functional and crosslinking monomers in the presence of AIBN as initiator. Also, the rebinding studies were carried out and different mathematical models, viz. Langmuir (L), Freundlich (F) and Langmuir–Freundlich (LF) were used: (i) for the evaluation of binding parameters; and (ii) for elucidation of the nature and type of bonding exist in IIPs. Thus, this paper highlights the characterization, analytical applications (preconcentration and selective separation) and rebinding studies of palladium(II) IIP particles synthesized by thermal polymerization using derivatives of quinoline as one of the ligand.

2. Experimental

2.1. Apparatus

A Shimadzu-UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan) was used for preconcentration and separation studies. A Perkin-Elmer A Analyst 100 atomic absorption spectrometer (Perkin-Elmer, USA) was used for measuring distribution ratios of copper, zinc and nickel during selectivity studies. A LI-120 digital pH meter (ELICO, India) was used for pH measurements. IR spectra were recorded in the range 4000–400 cm^{-1} using MAGNA FTIR-560 spectrometer (Nicolet, USA). The X-ray diffraction (XRD) patterns were obtained using Cu K_α X-ray source and Philips PW1710 diffractometer (Holland). The CHN-analysis was carried out using Perkin-Elmer elemental analyzer (Perkin-Elmer, USA).

2.2. Reagents

A stock solution of 1 mg ml^{-1} of palladium(II) was prepared by dissolving 0.1666 g of palladium chloride (99.9%, Loba Chemie, India) in 10 ml of 50% (v/v) HCl and diluted to 100 ml with deionized water. Rhodamine 6G (0.005%, w/v, Aldrich, USA) was prepared by dissolving 0.0125 g of reagent in 250 ml of deionized water. A citrate buffer (pH 4) was prepared by adjusting to 4.0 ± 1.0 after dissolving 8.4 g of citric acid (E-Merck, India) and 11.8 g of trisodium citrate (E-Merck, India) in 100 ml of deionized water. Potassium iodide (5%, w/v, E-Merck, India) was prepared by dissolving 5 g of KI in 100 ml of deionized water. 8-Aminoquinoline, 8-hydroxyquinoline, 8-mercaptoquinoline, 4-vinylpyridine (VP), 2-hydroxyethyl methacrylate, ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile were obtained from Aldrich (Milwauke, USA). All other chemicals used were of analytical reagent grade.

2.3. Preconcentration procedure

A portion of solution containing 2.5–100 (g of palladium was taken in 1-l beaker and diluted to 500 ml and the acidity of this solution was maintained at ∼0.5 N after addition of 20 ml of concentrated HCl. Palladium(II) IIP particles (0.05 g) prepared using AQ–VP ternary complex were added to above

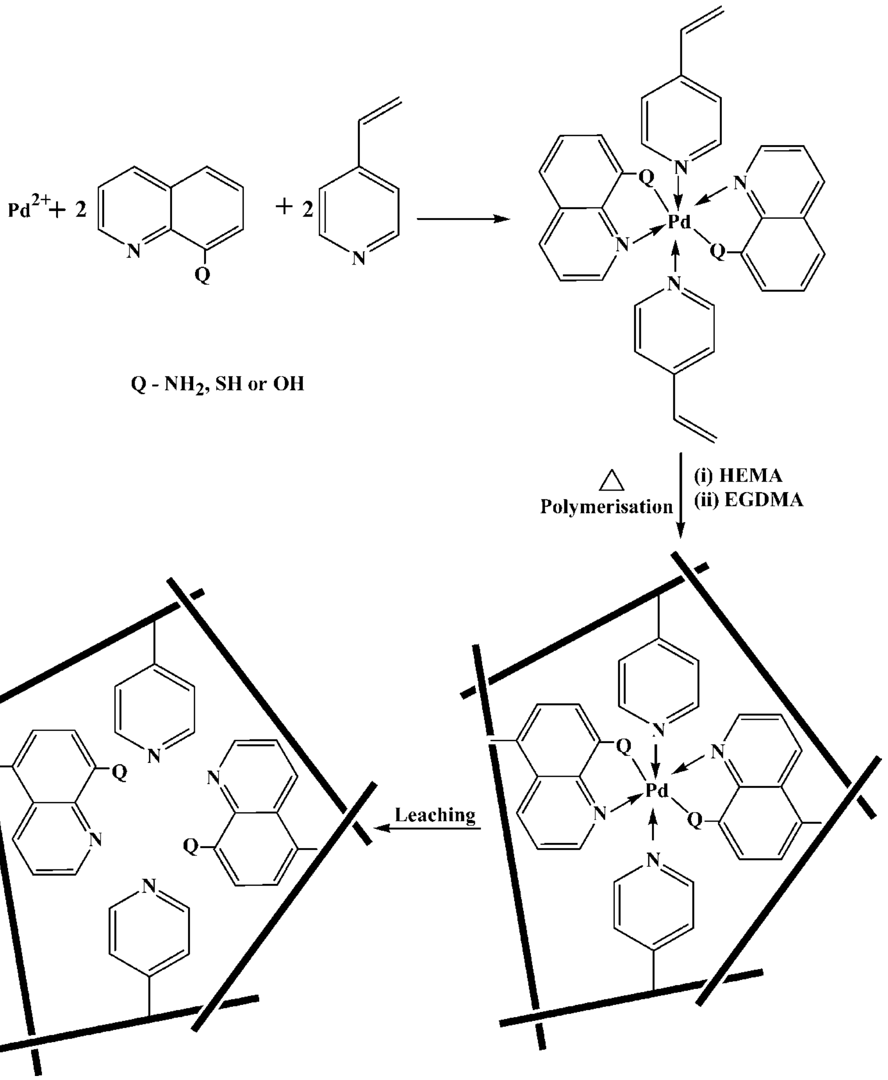

Fig. 1. Scheme for the preparation of palladium IIP materials.

solution and stirred for 30 min. The palladium(II) ions preconcentrated onto above IIP particles were eluted for 30 min with 2 × 10 ml of 50% (v/v) HCl. Suitable aliquots of the eluent were taken, pH was adjusted to 4.0 ± 1.0 after addition of 0.4 mol l^{-1} citrate buffer and palladium(II) content was established by employing iodide–rhodamine 6G procedure [13] reported elsewhere.

2.4. Constants

The constants, such as distribution ratio (*D*), percent extraction (%*E*) and selectivity coefficient ($S_{Pd^{2+}/M^{2+}}$) were defined elsewhere [14].

2.5. Ion-imprinted polymer (IIP) preparation

The synthesis of IIP materials was carried out in two steps as per the (Fig. 1) described elsewhere [15]. These include:

(1) preparation and isolation of ternary complexes of palladium with AQ–VP, HQ–VP and MQ–VP as ligands;
(2) copolymerization of the above ternary complexes with HEMA and EGDMA as functional and crosslinking monomers and 2-methoxy ethanol as porogen.

The solids thus formed after polymerization were dried in an oven at 80 °C for 2 h and sieved. The particles with sizes between 45–212 μm were collected.

2.6. Pretreatment of IIPs to leach imprint ion

The imprint ion, i.e. palladium(II) was leached from the above polymer materials by stirring with 100 ml of 50% (v/v) HCl for 18 h. The resultant polymer particles after filtration were dried in an oven at 80 °C to obtain IIP particles for possible preconcentrative separation of palladium(II) from dilute aqueous solutions.

2.7. Synthesis of respective control polymer particles (CPs)

CPs were prepared in a similar fashion as that of IIPs except that imprint ion, i.e. palladium was not added to the AQ- or HQ- or MQ-based recipes. The resulting CP materials were subjected to same pretreatment as in the case of IIPs to compare their performance: (i) for enrichment of palladium(II) from dilute aqueous solutions; and (ii) for separation of palladium(II) from selected inorganics.

2.8. Rebinding experiments

About 200 mg of the leached IIP particles was equilibriated with 94–3762 μmoles l-^{1} of palladium(II) as described in preconcentration procedure. The free concentration of palladdium(II) (F) was calculated using the equation

$$F = \frac{A_\mathrm{f} T}{A_\mathrm{t}} \qquad (1)$$

where T is the total concentration of palladium(II) ions. A_f and A_t are the blank corrected absorbance values of palladium(II) ion before and after the addition of palladium(II) IIP particles. The amount of analyte bound to the polymer (B) particles was calculated using the equation

$$B = T - F \qquad (2)$$

3. Results and discussion

8-Aminoquinoline is a selective spectrophotometric reagent for palladium wherein it forms yellow insoluble complex in weakly acidic solutions [16]. A number of transition and p-block elements were found not to interfere in the above determination. However, other noble metals particularly platinum and gold interfere when they exceed certain concentrations. We have shown recently palladium(II) IIP particles prepared, wherein Pd–dimethylglyoxime–VP complex is polymerized in the presence of styrene and divinyl benzene using AIBN as initiator, enabled better separation factors compared to platinum, copper, zinc and nickel [12]. In our quest to improve the separation factors of palladium with respect to other noble and transition elements, it is felt worthwhile to investigate various selective chelates of palladium, viz. 8-amino or 8-hydroxy or 8-mercaptoquinoline instead of DMG of the ternary complex during subsequent imprinting with a more efficient functional monomer such as HEMA and crosslinking monomer, viz. EGDMA. Table 1 gives the comparative account of percent enrichment and retention capacities of palladium(II) using CPs and IIPs prepared based on AQ, HQ and MQ ligands. As seen from the above table, AQ-based IIP particles alone gave quantitative enrichment of palladium(II) from dilute aqueous solutions. We now describe the characterization and analytical applications of AQ-based polymers synthesized as described elsewhere [15].

Table 1
Percent enrichment of 25 μg of palladium(II) present in 500 ml of solution onto 0.05 g of polymer particles (H^+ ∼0.5 N) and retention capacities

Polymer	Percent enrichment		Retention capacity (μg g^{-1} of polymer)	
	CP	IIP	CP	IIP
AQ	47.5	>99.0	26.10	28.82
HQ	49.0	66.2	26.91	27.51
MQ	40.4	68.1	25.14	27.70

3.1. Characterization studies

Since the percent extraction and selectivity coefficients of AQ-based IIPs were superior over other two (see Section 3.2.4), characterization studies were limited to AQ-based IIP only.

3.1.1. IR spectra

The IR spectra of control, unleached and leached IIPs were found to be almost similar which indicates that all the polymer particles have similar backbone.

The N–H stretching vibration at 3467 cm^{-1} in the leached IIP was shifted to 3441 cm^{-1} in the unleached material, indicating that the nitrogen of the –NH$_2$ group is involved in the metal bonding.

Also the C=N stretching vibration of the aromatic ring at 1268 cm^{-1} in the leached IIP was shifted to 1258 cm^{-1} in the unleached one due to the involvement of –N of the quinoline ring in the metal bonding. The vibration band of Pd–N usually occurs at 340 cm^{-1}. We didnot notice this band in IR spectra as we have scanning facility in the range 4000–400 cm^{-1} only.

The similarity in the standard IR spectra of 8-amino quinoline and that of leached IIP shows that the ligand is tightly intact in the polymer matrix even after leaching.

3.1.2. X-ray diffraction (XRD)

The XRD patterns of ternary complex, CP, unleached and leached amino quinoline-based IIP particles are given in Fig. 2. The peaks obtained at 2θ values 12.37, 18.92, 21.22, 28.20 and 32.85 in the Pd–AQ–VP ternary complex and unleached IIP were absent in the leached IIP indicating that all the palladium ions were completely removed during leaching and the XRD patterns of leached IIP were found to be exactly similar to that of the control polymer.

3.1.3. Microanalysis

The results obtained from the microanalysis studies of the unleached, leached and CP particles are given below.

Unleached, calculated (%): C→60.08; H→6.98; and N→1.05. Found (%): C→59.25; H→7.00; and N→1.59.
Leached, calculated (%): C→60.89; H→7.07; and N→1.06. Found (%): C→59.32; H→7.02; and N→1.23.
CP, calculated (%): C→60.89; H→7.07; N→1.06. Found (%): C→59.30; H→7.03; N→1.20.

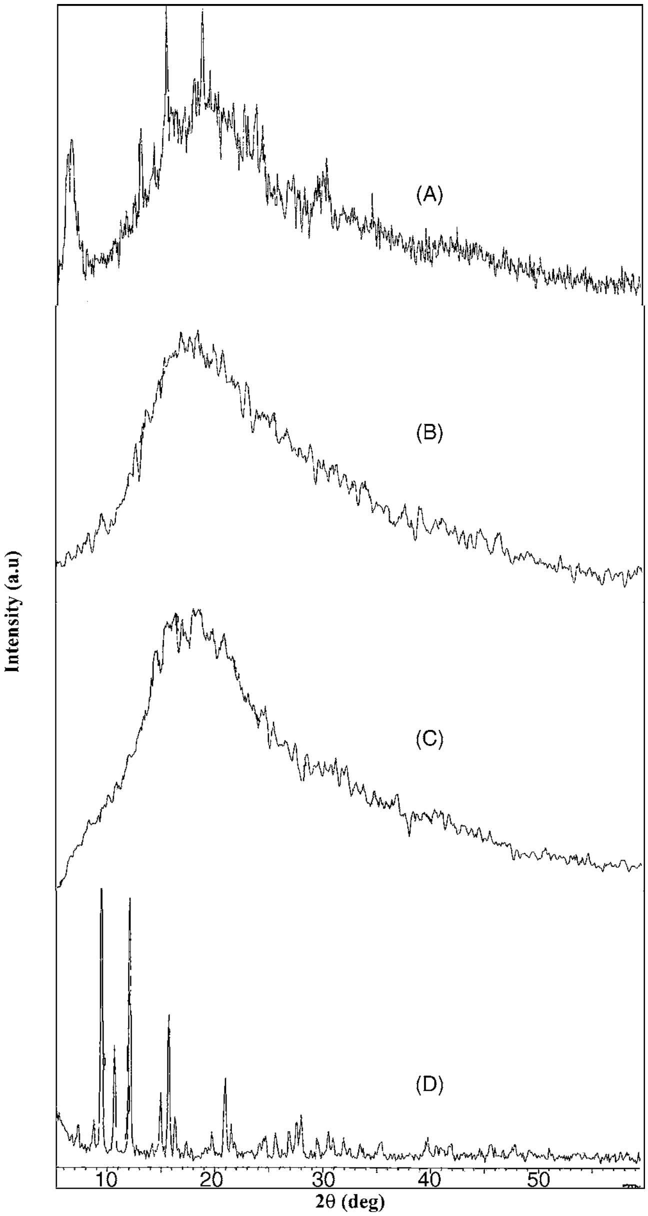

Fig. 2. XRD patterns of unleached (curve A); leached (curve B) palladium(II) IIP particles; CP (curve C); and Pd–AQ–VP ternary complex (curve D).

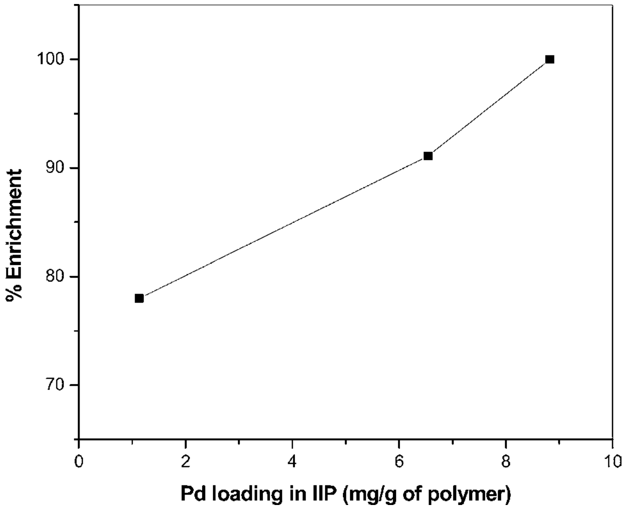

Fig. 3. Effect of palladium loading in unleached IIP particles (mg of Pd^{2+} per g of polymer) on percent extraction of Pd^{2+} with leached IIP particles.

The microanalysis studies reveals that during the leaching of IIP particles, only the palladium(II) ions were removed and not the ligands.

3.2. Analytical studies

3.2.1. Preconcentration studies

Preconcentration studies were carried out by varying the palladium loading of unleached IIP (AQ-based) using 2-methoxy ethanol as porogen. The resulting polymer materials were leached with 50 ml of 50% (v/v) HCl for 18 h, filtered and dried to obtain leached IIP particles. The enrichment studies were carried out by following the procedure described in Section 2.3. The results obtained were shown in Fig. 3 from which it is clear that by increasing palladium(II) loading to 8.82 mg of Pd^{2+} g^{-1} of unleached IIP, the quantitative recovery of palladium ion using leached IIP particles from aqueous solution is possible. This observation is attributed to the availability of more and more number of binding sites per gram of the leached IIP particles.

3.2.2. Optimization of sorption and elution of palladium ions using AQ-based IIP particles

A set of solutions (volume = 500 ml) containing 25 μg of palladium(II) ions were taken and acidity was varied between 10^{-4}–1.0N in HCl and the recommended procedure was followed. The enrichment of palladium is constant and maximum in the acidity range of 10^{-4}–0.5N of HCl (see Table 2) which is expected in view of the maximum stability of Pd–AQ–VP complex [16]. In all subsequent work, the acidity was maintained at $\sim$0.5N by adding 20 ml of concentrated HCl. The percent enrichment of palladium(II) ion by using CP particles is also shown in Table 2 for comparison, which indicates the imprinting effect in all instances.

The influence of weight of polymer particles (IIP or CP) on the percent enrichment of 25 μg of palladium(II) present in 500 ml of solution was systematically investigated. The results obtained are compiled in Table 2, from which it is seen that: (i) for quantitative preconcentration, a minimum of 0.025 g of palladium(II) IIP particles are required; and (ii) imprinting effect is noticed in all instances once again. Hence, 0.05 g of palladium(II) IIP (AQ) was used for subsequent preconcentration studies. As seen from Table 2, a minimum of 25 min of stirring is necessary to quantitatively preconcentrate 25 μg of palladium(II) present in 500 ml of solution using 0.05 g of palladium(II) IIP particles. Further, it was established that stirring for 30 min with 2 × 10 ml of 50% (v/v) HCl is necessary (see Table 2) for quantitative elu-

Table 2
Influence of various parameters on the percent enrichment/extraction of palladium(II) onto AQ-based CP and IIP particles

	Percent extraction	
	CP	IIP
HCl (N)		
1.0	12.35	82.92
0.5	36.4	>99
0.1	47.5	>99
0.01	47.5	>99
0.001	47.5	>99
0.0001	42.2	54.2
Weight of IIP (g)		
0.01	40.6	60.8
0.025	42.8	>99
0.05	45.8	>99
0.15	47.2	>99
0.25	47.5	>99
Preconcentration time (min)		
10	30.5	50.7
20	40.0	62.5
25	45.5	98.0
30	45.5	>99
Elution time (min)		
10	40.0	64.25
20	43.0	95.3
30	45.5	>99
Eluent volume (ml)		
2 × 10	45.5	>99
2 × 15	45.8	>99
2 × 20	45.6	>99
Aqueous phase volume (ml)		
25	45.2	>99
50	45.8	>99
100	45.5	>99
500	45.0	>99
1000	40.0	63.5

0.05 g of CP/IIP H^+ ∼0.5 N; preconcentration time = 30 min; elution time = 30 min; eluent volume = 2 × 10 ml; and aqueous phase volume = 500 ml.

tion of palladium(II) sorbed on palladium(II) IIP particles. The change of aqueous phase volume from 25 to 1000 ml indicates that the preconcentration efficiency was unaffected upto 500 ml (see Table 2).

The retention/binding capacities of CP and IIP particles were determined by saturating 0.02 g of polymer material with 1 mg of palladium(II) under optimal conditions as described above. The amounts of palladium(II) sorbed on polymer particles was determined spectrophotometrically after eluting with 2 × 10 ml of 50% (v/v) HCl. The results obtained (as shown in Table 1) indicate that the retention capacities are: (i) slightly higher for IIP particles compared to CP particles; and (ii) are in the same order for AQ- or HQ- or MQ-based IIPs. This result indicate that the enrichment by HQ- and MQ-based IIPs are kinetically slower compared to AQ-based IIPs, as the percent extraction of palladium is lower in case of HQ- and MQ-based IIPs (see Table 1).

3.2.3. *Statistical and calibration parameters*

Under the optimum conditions described above, the calibration curve was linear over the concentration range of 2.5–100 μg of palladium(II) present in 500 ml of solution. Five replicate determinations of 25 μg of palladium(II) in 500 ml of solution gave a mean absorbance of 0.104 with a relative standard deviation of 2.25%. The detection limit corresponding to three times the standard deviation of the blank was found to be 5.0 μg l^{-1}. The linear equation with regression is as follows

$$A = (0.01953 \times C) - 0.0123$$

$$\text{Correlation coefficient} = 0.99999 \qquad (3)$$

where A is the absorbance and C is the amount of palladium in micrograms per one litre of sample solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

3.2.4. *Selectivity studies*

The percent extraction and distribution ratios of palladium, platinum, gold, copper, zinc and nickel ratios and selectivity coefficients of palladium(II) with respect to the above mentioned elements were determined by using AQ- or HQ- or MQ-based CP and IIP particles and the results obtained are compiled in Table 3.

The following observations can be made from Table 3

(i) CP particles show minimal selectivity for palladium over gold and platinum;
(ii) on imprinting, the selectivity coefficients increases with AQ-, HQ- and MQ-based polymers;
(iii) the increase in selectivity is in the order: AQ > HQ > MQ;
(iv) even though the selectivity coefficients of palladium over platinum are 4.40 and 3.03 in case CP particles of AQ–VP and DMG–VP complexes, AQ-based IIP particles gives $\beta_{\mathrm{Pd}^{2+}/\mathrm{Pt}^{4+}}$ of 5500 compared to 521 with DMG-based IIP particles [12];
(v) the CP particles AQ, HQ or MQ based IIPs showed good selectivity for palladium(II) compared to base metals such as copper(II), zinc(II) and nickel(II), which usually coexist with palladium in its mineral deposits;
(vi) on imprinting, the selectivity coefficients of palladium over base metals improve further by about 100–400-fold.

Table 4 shows the percent extraction, distribution ratios and selectivity coefficients of palladium(II) with respect to the above base metals, when present in admixtures, in case of AQ-, HQ- or MQ-based IIP particles. It is clear from Table 4 that the selectivity coefficients of palladium(II) over base metals are same, when they are present individually or in admixtures.

Table 3
Percent extraction, distribution ratio and selectivity coefficients ($\beta_{\mathrm{Pd}^{2+}/\mathrm{M}^{n+}}$) of leached CP and IIP particles

Element	Percent extraction		Distribution ratio		Selectivity coefficient ($S_{\mathrm{Pd}^{2+}/\mathrm{M}^{n+}}$)	
	CP	IIP	CP	IIP	CP	IIP
Pd						
AQ	45.5	>99	0.904	99	–	–
HQ	49.02	66.19	0.960	1.956	–	–
MQ	40.38	68.06	0.677	2.130	–	–
Pt						
AQ	17.04	1.79	0.205	0.018	4.40	5500
HQ	24.10	31.66	0.317	0.460	3.02	14.25
MQ	32	20.9	0.470	0.260	1.44	8.19
Au						
AQ	77.5	12.8	3.450	0.146	0.26	674.2
HQ	73.07	5.33	2.710	0.0563	0.35	34.70
MQ	58.2	31.15	1.394	0.452	0.485	4.710
Cu						
AQ	0.02	0.01	12.0×10^{-4}	1.0×10^{-4}	0.45×10^{4}	1×10^{6}
HQ	0.01	0.01	1.0×10^{-4}	11.0×10^{-4}	0.90×10^{4}	1×10^{6}
MQ	0.01	0.01	1.0×10^{-4}	11.0×10^{-4}	0.90×10^{4}	1×10^{6}
Zn						
AQ	0.02	0.01	2.0×10^{-4}	1.0×10^{-4}	0.45×10^{4}	1×10^{6}
HQ	0.01	0.01	1.0×10^{-4}	1.0×10^{-4}	0.90×10^{4}	1×10^{6}
MQ	0.03	0.01	3.0×10^{-4}	1.0×10^{-4}	0.30×10^{4}	1×10^{6}
Ni						
AQ	0.09	0.01	9.0×10^{-4}	1.0×10^{-4}	0.1×10^{4}	1×10^{6}
HQ	0.01	0.01	1.0×10^{-4}	1.0×10^{-4}	0.9×10^{4}	1×10^{6}
MQ	0.04	0.01	4.0×10^{-4}	1.0×10^{-4}	0.2×10^{4}	1×10^{6}

3.3. Adsorption studies

A binding isotherm measures the binding efficiency of a polymer over a range of analyte concentrations. The binding parameters such as total number of binding sites (N_t), median binding affinity constant (K_o), heterogeneity index (m) and binding capacity ($N_t \times a$), etc can be calculated from the binding isotherms by fitting the experimental adsorption isotherm to specific binding models. As in case of MIPs [17–19], experimental binding isotherm were obtained for AQ-, HQ- and MQ-based IIP particles by equilibrating with known concentration of palladium over the range as described in Section 2.8. The Scatchard plots as well as Langmuir, Freundlich and Langmuir–Freundlich plots were employed in this paper to compare AQ-, HQ- and MQ-based palladium IIPs.

3.3.1. Scatchard plots

The conventional form of utilizing scatchard plot to generate the binding parameters require a plot of B/F versus B. For homogeneous systems that contain only one type of binding site, the scatchard plot yield a straight line with a slope equal to the negative of the binding affinity (K_o) and the X-intercept equal to the number of binding sites (N_t). For AQ polymer, the scatchard plot gives a straight line with N_t and K_o values of 963.766 and 24.80, respectively. In contrast, the scatchard plots for the HQ- and MQ-based IIPs were curved as observed for most MIPs. This curvature has been cited as evidence for binding site heterogeneity. Heterogeneity can be incorporated into the scatchard plot analysis by modeling the curved isotherm as two or more straight lines, normally done by using bi, tri or tetra Langmuir models. However, the number of tangents to be drawn and finding the positions for the tangents is a cumbersome task. Moreover, this analysis is based on a series of approximations and the estimates of the binding parameters will be accurate only under certain conditions; and thus the results often lead to ambiguous conclusions. From the limiting slope analysis of straight lines, the curved lines yield more than one set of binding parameter

Table 4
Percent extraction, distribution ratio and selectivity coefficients ($S_{\mathrm{Pd}^{2+}/\mathrm{M}^{n+}}$) from admixtures of palladium, copper, zinc and nickel using IIP particles

	Percent extraction			Distribution ratio × 10^4			Selectivity coefficient × 10^6 ($\beta_{\mathrm{Pd}^{2+}/\mathrm{M}^{n+}}$)		
	Cu	Zn	Ni	Cu	Zn	Ni	Cu	Zn	Ni
AQ IIP	0.01	0.01	0.01	1.0	1.0	1.0	1	1	1
HQ IIP	0.02	0.01	0.02	2.0	1.0	2.0	0.5	1	0.5
MQ IIP	0.01	0.09	0.01	1.0	9.0	1.0	1	0.9	1

corresponding to the high and low affinity sites. Thus, complications quickly arise while using this analysis to compare different polymers [20].

3.3.2. Binding isotherm studies

Batch rebinding studies represents a key method for characterizing and comparing imprinted polymers. The binding parameters can be estimated from the binding isotherms using various mathematical models. However, in the choice of the proper model, many important features should be taken into account, apart from the numerical complexities involved in the fitting procedure. The important among them are that the model should be thermodynamically sound and have a clear physical meaning, limiting the introduction of supplemental parameters to the bare necessities. Many isotherms have been reported in the literature to calculate the binding properties of MIPs. However, the most commonly used models were Langmuir, Freundlich and Langmuir–Freundlich.

The LF isotherm can be given as

$$B = \frac{N_t a F^m}{1 + a F^m} \tag{4}$$

where N_t is the number of binding sites, a is related to the median binding constant K_o ($K_o = a^{1/m}$) and m is the heterogeneity index. For a homogeneous material, m is equal to 1, whereas when m is between 0 and 1, the material is heterogeneous. For homogeneous material ($m = 1$), the LF isotherm reduces to the Langmuir isotherm

$$B = \frac{N_t a F}{1 + a F} \tag{5}$$

and on the other hand as either F or a approaches 0, the LF isotherm reduce to the Freundlich isotherm

$$B = a\ F^m \tag{6}$$

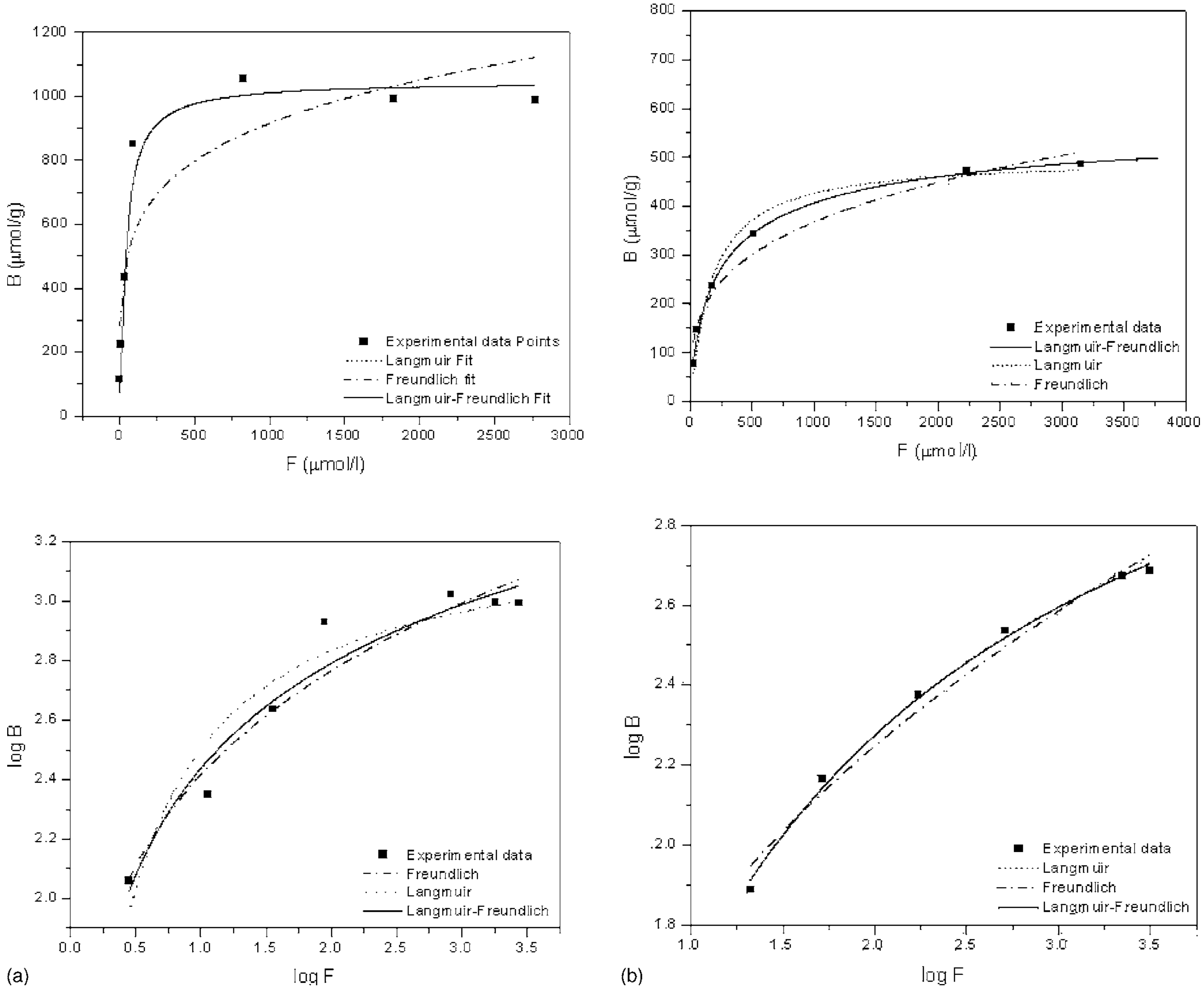

Fig. 4. Normal (top) and log plots (bottom) of adsorption isotherms for palladium(II) with: (a) AQ; (b) HQ; and (c) MQ-based palladium(II) IIP particles. The experimental data (■) were fit to the Langmuir (L) (dotted line); Freundlich (F) (dash–dot line) and LF (solid line) isotherms.

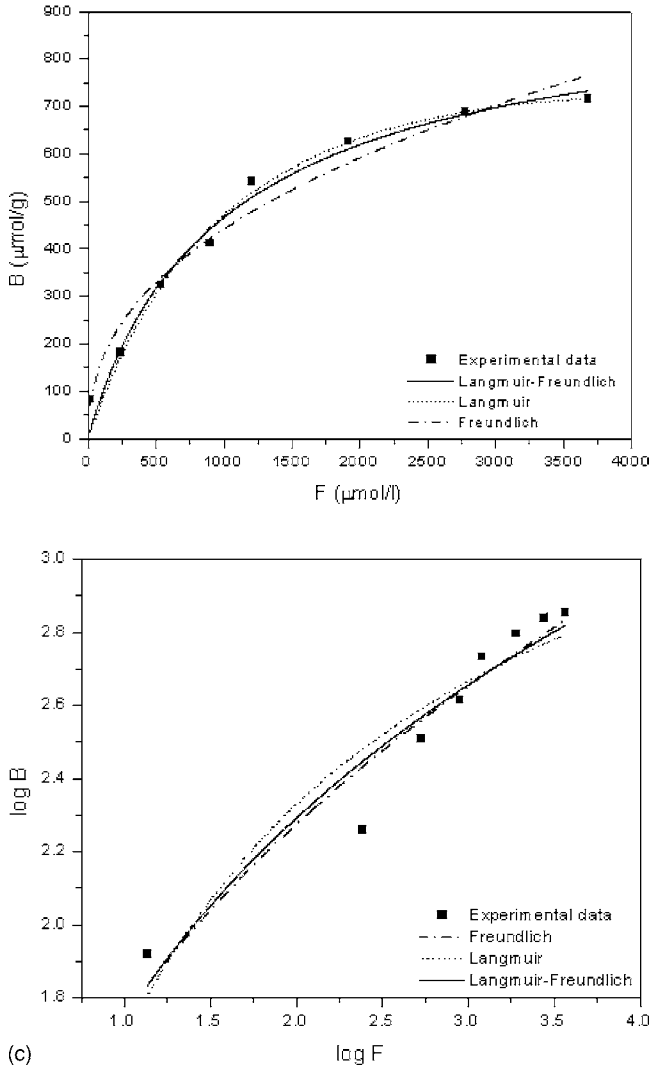

Fig. 4. (*Continued*).

In the present study, the isotherm data were fitted to the above three isotherm models, (i.e.) the Langmuir, Freundlich and Langmuir–Freundlich models. The *B* versus *F* and log*B* versus log*F* plots obtained are shown in Fig. 4. The isotherm model parameters were obtained by a non-linear least square fitting of the experimental data using Marquardt–Levenberg algorithm in Microcal Origin 6.0® (Microcal Software Inc., 2000) data analysis package. The following function is minimised in order to obtain the best coefficients for the isotherm parameters

$$F^2 = \frac{\sum_{i=1}^{N} (X_i^{\text{exp}} - X_i^{\text{th}})^2}{X_i^{\text{th}}} \tag{7}$$

where, *N* is the number of data points, X_i^{exp} and X_i^{th} are the experimental data points and the points corresponding to the model. To avoid being trapped in local minima, which give incorrect results, the fitting was carried out several times using different initial guess values for the isotherm parameters. The coefficient of determination (R^2) values for the adsorption isotherms was also found out. The isotherm that correlates better with the experimental data is the one that exhibits the R^2 value closer to 1. The fitting coefficients or binding parameters obtained by fitting L, F and LF curves to the experimental adsorption isotherms of palladium(II) IIP particles are shown in Table 5.

Comparing the suitability of isotherms in fitting the adsorption data, the LF isotherm seems to provide better fits for the three IIPs [21–23]. It does explain the degree of heterogeneity of the IIP in an explicit manner. Considering the values of (R^2) calculated for the IIPs, it is quite clear that the AQ-based IIP shows good agreement with the homogeneous distribution of binding sites and so it gives high selectivity and percent extraction compared to other two IIPs. Even though the MQ-based IIP had a higher number of binding sites (N_t) than the AQ-based IIP, it is the heterogeneity of the polymer that causes a reduction in selectivity and percent extraction due to the lack of accessibility of the sites. The decrease in selectivity and percent extraction for HQ-based IIP can be attributed to the less number of binding sites and lower *m* value. It should be pointed out that heterogeneity is normally detrimental to the binding properties, temper and limits the capacity and selectivity of IIPs. Also from the Table 5, it is clear that the variable '*a*' that is relating to the median binding affinity is higher for the AQ-based IIP compared to the other two IIPs, which is in agreement with the stability of the complexes of palladium(II) ion with different donor atoms of the ligands.

Martin–Esteban group have calculated fitting parameters using LF model for propazine and [24] and fenuron [25] with MAA–EGDMA molecular-imprinted polymers via bulk and precipitation polymerization. Umpleby et al. [21] have found LF model is uniquely suited to fit isotherms and to calculate the fitting parameters for covalent (MIP 1), non-covalent (MIP 2) in addition to the other three MIPs (MIP 3–MIP 5) based on the literature data. Table 6 lists the N_t and $K_\text{o}$values obtained by Martin–Esteban and Umpleby et al. for MIPs along with our data for AQ-, HQ- and MQ-based palladium(II) IIPs. As seen from the Table 6, the N_t values are higher for IIPs compared to MIPs excepting MIP 2. The high value for MIP 2 is an exception which can be attributed to the high heterogeneity of this polymer. Similarly, the mean association constants for palladium(II) IIPs lie between two extremes characterized by MIP 1 and MIP 2.

The accuracy of the calculated fitting parameters must be evaluated regarding the concentration range studied, i.e. the binding curves have to be measured over a wide concentration range (covering both saturation and subsaturation regions) which is assessed if K_o falls between the limits $1/F_\text{max}$ and $1/F_\text{min}$, as reported elsewhere [24]. From the table, it is clear that the K_o falls within the required limits.

3.3.3. *Affinity distribution studies*

To address the heterogeneity in IIPs and for the accurate comparison of the binding properties, we have calculated the affinity distribution of the AQ-, HQ- and MQ-based IIPs. An

Table 5
Fitting parameters for the F, L and LF fit to the experimental adsorption isotherms of studied IIPs[a]

Fitting parameters	Isotherm models								
	F			L			LF		
	AQ	MQ	HQ	AQ	MQ	HQ	AQ	MQ	HQ
N_t (μmol g^{-1})	–	–	–	1048.14	922.0	500.22	1048.2	1161.29	593.61
a (m mol^{-1})	231.50	23.92	50.36	0.027	0.0028	0.0057	0.0274	0.0032	0.0215
Binding capacity ($N_t \times a$)	–	–	–	28.708	2.6277	2.886	28.720	3.727	12.786
m	0.199	0.422	0.287	–	–	–	0.9998	0.69522	0.66843
K_o (m mol^{-1})	–	–	–	–	–	–	0.02738	2.590×10^{-4}	3.2102×10^{-3}
K limits (m mol^{-1})[b]	–	–	–	–	–	–	3.607×10^{-4}–0.3534	2.5716×10^{-4}–0.0733	3.1717×10^{-3}–0.0472
R^2	0.80537	0.93676	0.96790	0.97123	0.88799	0.98060	0.97123	0.93667	0.99888

[a] The fitting coefficients are mean values calculated from three independent experimental binding isotherms. The relative standard deviation obtained for each coefficient was lower than 10%.

[b] Calculated from experimental maximum and minimum free analyte concentration ($F_{\max}$ and $F_{\min}$) by the relationships $K_{\min} = 1/F_{\max}$ and $K_{\max} = 1/F_{\min}$.

Table 6
N_t and K_o values of various imprinted polymers

Polymer	N_t	K_o	Reference
Propazine	0.18	86	[24]
Fenuron	35	0.18	[25]
MIP 1	120	1.4	[21]
MIP 2	8×10^5	1.97×10^{-9}	[21]
MIP 3	23	1.4×10^4	[21]
MIP 4	126	2.168	[21]
MIP 5	58	5.9×10^{-6}	[21]
IIP (AQ)	1048	2.74×10^{-2}	Present study
IIP (HQ)	593.6	3.21×10^{-3}	
IIP (MQ)	1161.3	2.59×10^{-4}	

affinity distribution is a plot of the number of binding sites (N_i) against the association constant (K_i). In the present study, LF isotherm seems to be the most applicable isotherm among the three isotherm models as seen from above comparisons as it can model both the saturation and sub saturation behaviour. Hence, we have limited to generation of the affinity distribution curves corresponding to LF isotherm alone. (see Fig. 5). The affinity distribution expression for the LF isotherm as derived by Umpleby II et al. [21] is used for plotting the affinity distribution curve. The expression is given by

$$N_i = N_t a m \left(\frac{1}{K_i}\right)^m \times \left(\frac{1 + 2a(1/K_i)^m + a^2(1/K_i)^{2m} + 4a(1/K_i)^m m^2 - a^2(1/K_i)^{2m} m^2 - m^2}{[1 + a(1/K_i)^m]^4}\right) \quad (8)$$

The earlier literature [21] shows that the covalently imprinted polymers gave a relatively homogeneous unimodal distribution in the affinity spectrum whereas the non-covalently imprinted polymers displayed a heterogeneous distribution with an asymptotically decaying shape.

The affinity distribution plots for AQ- and HQ-based IIPs show that the rebinding takes place in a covalent mode. From the affinity distribution curves for AQ and HQ (Fig. 5a and b), it can be seen that the peak of the distribution is centered at $K_o = a^{1/m}$. Also the shape of the distribution gets broadened as the heterogeneity index reduces to lower values from 1. On the other hand, the affinity distribution plot for MQ based IIP shows that the rebinding takes place in non-covalent mode (see Fig. 5c). The tailing portion corresponds to the lower concentration, and in this case it is very difficult to reach the saturation due to the heterogeneity. Generally, the stability of the metal complexes (pK_{HB}) having N, O and S as donor atoms decreases in the order N < O < S. But elements which have a particular tendency to form donor π bonds (Hg, Pt, Pd and Ag, etc) show the reverse order N > O > S for the change in stability [26]. The results obtained in the present investigation is in tune with this observation as the AQ-based polymer showed higher selec-

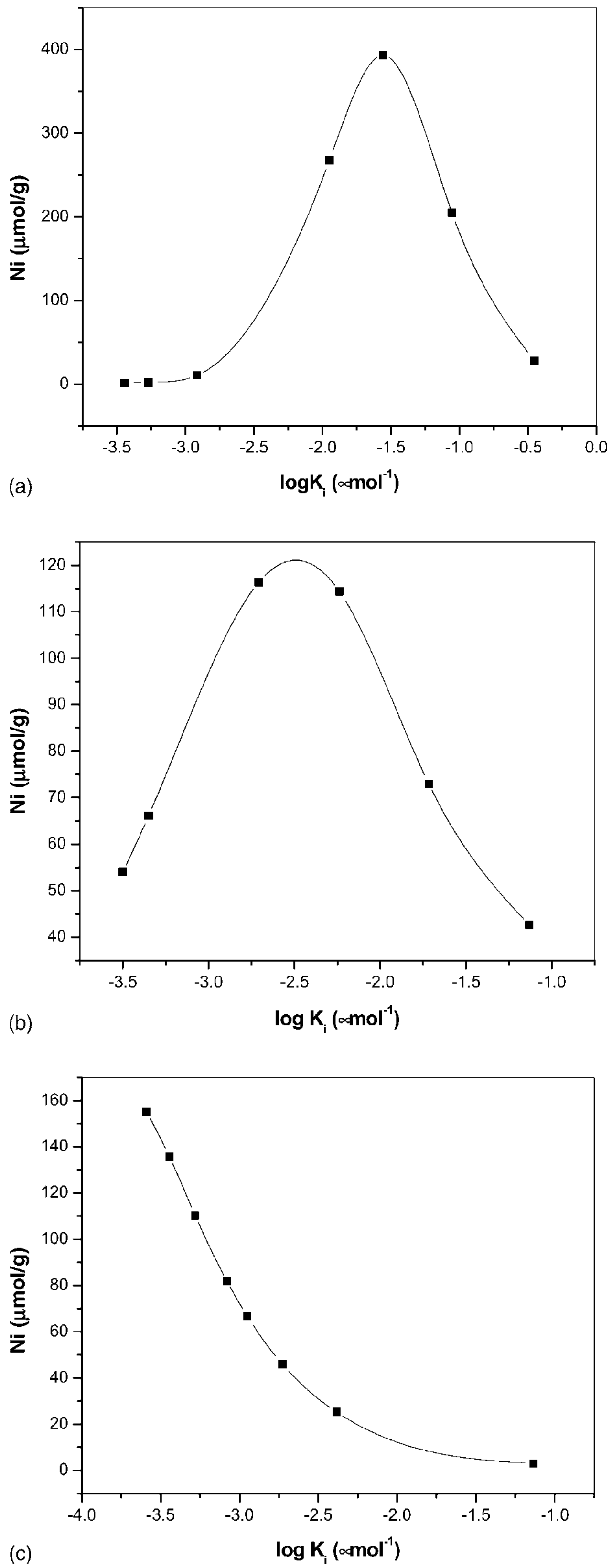

Fig. 5. Affinity distribution curves for (a) AQ; (b) HQ; and (c) MQ palladium(II) IIP particles calculated using Eq. (8).

tivity and percent extraction compared to HQ- and MQ-based IIPs.

3.4. Reuse studies

The palladium(II) IIP particles were subjected to repeated preconcentration and elution steps to check the reusability. The retention/binding capacities of palladium(II) IIP particles were fairly constant even after 10 cycles. These studies clearly indicate the availability of reversible nature of binding sites for picking palladium(II) ions using palladium(II) IIP particles.

4. Conclusions

Palladium(II) IIP particles were synthesized as per the procedure described elsewhere [15] using the ternary complex of palladium(II) with AQ, HQ or MQ as one of the ligand and 4-vinyl pyridine as other ligand. Even though, imprinting effect was noticed with AQ, HQ- and MQ-based palladium(II) IIP particles, the AQ-based IIP particles showed better preconcentration efficiency and higher selectivity coefficient compared to selected noble and base metals. Furthermore, the rebinding experiments enabled the: (i) evaluation of binding parameters; and (ii) elucidation of nature and type of bonding present in IIPs. These results show that LF isotherm model fits well with experimental adsorption isotherm compared to L or F model. The affinity distribution curve indicates that rebinding takes place via covalent mode in case of AQ- and HQ-based palladium(II) IIP particles while in MQ-based particles it is via non-covalent mode. Studies are in progress to demonstrate the wide applicability of these models to other IIP particles also. Such studies may open new vistas in understanding the ion recognition mechanism which will no doubt open up new directions in the synthesis of tailor made IIPs for various inorganic ions in the near future.

Acknowledgement

The authors, Sobhi Daniel and Prem E. J. Babu are thankful to the CSIR, New Delhi, India for the award of Junior and Senior Research Fellowships, respectively.

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