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ORIGINAL PAPER

The Pre-concentration and determination of Iridium and Palladium in environmental water by imprinted polymer-based method

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Abstract In this study, the imprinted aniline–formaldehyde was used as an adsorbent for removal of Iridium and Palladium ions from aqueous solutions through batch equilibrium. The sorbent was characterized by fourier transform infrared spectroscopy. The influence of pH, equilibrium time, temperature and initial concentration of metal ions on adsorbed amount of both ions were investigated. The maximum adsorption capacity in initial concentration of 100 mg/L was found to be 12.5 mg/g at pH 7.0 and 14.3 mg/g at pH 8.0 for Iridium and Palladium, respectively. In addition, the best desorption of the metal ions from resin was obtained by 0.5 mol/L nitric acid as eluting agent. The profile of both ions uptake on this sorbent reflects good accessibility of the chelating sites in the imprinted aniline–formaldehyde. Langmuir, Freundlich, Temkin and Redlich–Peterson isotherm models were applied to analyze the experimental data. Moreover, Langmuir linear method was used to obtain the isotherm parameters. However, Langmuir type II achieved the highest coefficient which led to the best fit for the palladium and the best fit for Iridium obtained from linear Redlich–Peterson. However, the thermodynamic parameters (ΔG°, ΔH°, and ΔS°) were also determined using the equilibrium constant values obtained at different temperatures. The results showed that the adsorption for Iridium and Palladium ions was spontaneous nature and endothermic. Moreover, the method was applied for the determination of both ions from tap water samples.

Keywords Adsorption isotherms · Error analysis · Kinetic studies

Introduction

Palladium is a rare and lustrous silvery white metal and was discovered in 1803 by William Hyde Wollaston. Palladium, platinum, rhodium, ruthenium, Iridium and osmium form a group of elements referred to as the platinum group metals (PGMs). They have similar chemical properties, but palladium has less melting point and dense. Moreover, the unique properties of palladium and other platinum group metals account for their widespread usage. A quarter of all goods manufactured today either contains PGMs or have a significant part in their manufacturing process played by PGMs (Lide and Frederikse 1995). Moreover, Palladium is found in many electronics such as computers, mobile phones, multi-layer ceramic capacitors, component plating and low voltage electrical contacts. Palladium is also used in dentistry, medicine, hydrogen purification, chemical applications and groundwater treatment. It plays a key role in the technology used for fuel cells, which combine hydrogen and oxygen to produce electricity, heat and water (Anand 1997; Eagleson 1988; Kenneth Brady 2011).

Iridium is a very hard, brittle and silvery white transition metal of the Platinum family, whereas Iridium is the second densest element and one of the most corrosion-

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resistant metal even at the temperatures as high as 2,000 °C. The most important Iridium compounds are the salts and acids which are formed by chlorine, though Iridium also forms a number of organometallic compounds used in industrial catalysis and in research. Iridium metal is employed when high corrosion resistance at high temperatures is needed (Lide and Frederikse 1995; Anand 1997; Eagleson 1988).

The literature review of the previous studies of the research shows the determination of Ir, and Pd are the most developed among PGE determination techniques. A number of highly sensitive and powerful techniques are available such as inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry (IDMS), stripping voltammetry (SV), neutron activation analysis (NAA), electrothermal (graphite furnace) atomic absorption spectrometry (ETAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Amut et al. 2010). The last two methods can only be applied to environmental samples in combination with pre-concentration. Together with ICP-MS and NAA, SV is the most sensitive technique for measuring PGE. The determination of Pd is known to be highly sophisticated. The determination of Pd by ICP-MS is strongly hampered by numerous interferences, making an accurate analysis without tedious manipulations such as matrix separation or/and mathematical correction procedures impossible (Zereini and Alt 1999; Krachler et al. 1998).

In fact, XRF techniques are commonly used for noble metal determinations in industrial applications (Beary and Paulsen1995). Ion-imprinted polymers are prepared by the copolymerization of functional and cross-linking monomers in presence of toxic target inorganic species (the imprint ion) which act as ionic templates. The functional groups are held in position by the highly cross-linked polymeric structure. Subsequent leaching of imprint ion reveals binding sites that are complimentary in size and shape to the imprint ion (Booking 2007). Ion imprinting polymers (IIPs) have outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare. Hence, IIPs are currently being explored for their catalytic applications, stationary phases in chromatographic and flow-injection columns, membrane separations and developing sensors (Prasada Rao et al. 2004). Although the bases of the ion imprinting polymer technique were explained a few years ago, the technique is still applied for heavy metal extraction (Bruno et al. 2006; Ivanka et al. 2009; He et al. 2006; Liu et al. 2005; Li et al. 2007a, b). Molecular imprinting is a method that enables the formation of tailor-made recognition materials by copolymerizing suitable monomers in the presence of a desired print molecule (Yilmaz et al. 2002; Kugimiya et al. 1998; Jin and Ho 2005; Su et al. 2008; Li et al. 2007a, b; Pap and Horvai 2004; Lei and Tan 2002; Amut et al. 2010; Kubo et al. 2004; Kandimalla 2004; Andersson 2000; Asanuma et al. 2001; Cirillo et al. 2010; Matsui et al. 2004; Shiigi et al. 2003; Caro et al. 2006; Zhang et al. 2009; Pichon 2007). Recently, there are some reports on the application of imprinted technique for separation and enrichment of heavy metal ions (Birlik et al. 2007; Baghel et al. 2007). Among present ion-imprinted technologies, imprinting a matrix with binding sites situated at the surface has many advantages including the following: the sites are more accessible, mass transfer is faster and the binding kinetics is faster (Yang et al. 2005). The sol–gel process can be described as the creation of an oxide network by progressive poly-condensation reactions of molecular precursors in a liquid medium. The surface ion-imprinted technique in combination with sol–gel process can easily synthesize a high cross-linking and better thermal stability and chemical stability material; on the other hand, the specific chemical functional groups inducted into the network structure can improve selectivity and specificity to template. Thus, this technology provides a new platform to prepare high-performance ion-imprinted polymers (Li et al. 2007a, b; Elena et al. 2005).Our new imprinted polymer and method have several advantages (I) simple operation (II) less time for polymer synthesis (III) rapid phase separation (IV) high selectivity by the polymer memory effect toward the metal ion interaction (V) lower cost (VI) the capability to combine with different detection techniques.

Materials and methods

Aniline, formaldehyde, hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, acetic acid, sodium acetate, sodium dihydrogen phosphate, disodiumhydrogen phosphate, acetone, ethanol and other materials are used in the experiments which are the Merck's products (Darmstadt, Germany). Moreover, all the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (100 mg/L) of Ir(III) and Palladium were prepared by dissolving appropriate amounts of $Ir(Cl)_3$ in deionized water and Palladium bar with purity of 99.9 %; hydrochloric acid and nitric acid (Merckt Company) and deionized water were used for the preparation of metal solution, and 0.1 M acetic acid–acetate buffer (pH = 3–6.5) and 0.01 M phosphate buffer (pH = 6.5–9) were used to adjust the pH of the solutions, wherever it was suitable. Moreover, Iridium and Palladium concentrations of the samples were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared

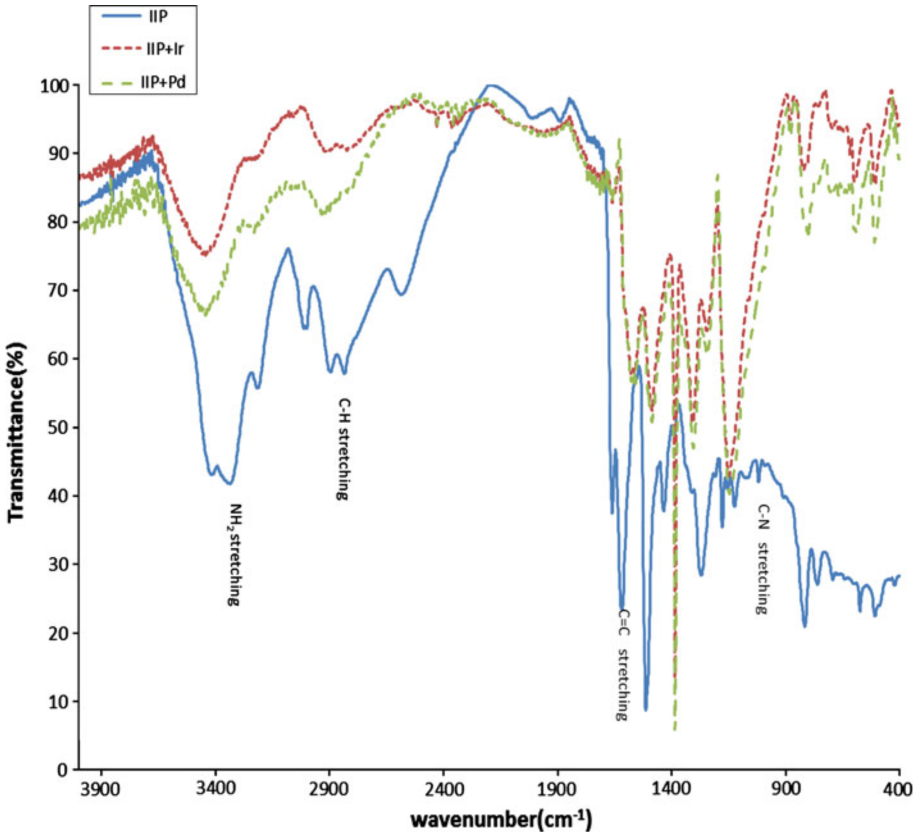

Fig. 1 FT-IR spectrum of IIP, IIP loaded Iridium and IIP loaded Palladium

spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland) by the potassium bromide pellet method.

Synthesis of aniline-formaldehyde polymer

Synthesis of AFC

Commercial grade aniline ($C_6H_5NH_2$) for synthesizing polymers was purified by distilling over KOH pellets at 180 °C. Moreover, boiling point AFC (Aniline Formaldehyde Condensate) was synthesized by reacting formaldehyde (37 %) with aniline as described in the literature (Albino Kumar et al. 2007).

Besides, $Ir(Cl)_3$ and Pd (elementary palladium metal) were used as the source of Iridium and Palladium. In a 100-mL reaction vessel, 5 mL of 37 % formaldehyde was added to a mixture of 9.3 g of aniline and 3 mL of 37 % HCl. Condensation was carried at 100 °C for 2 h. Then, the temperature was decreased to 60 °C and the mixture was neutralized with 4 mL of 30 % NaOH, resulting in an insoluble liquid resin. After that, the resin was washed with warm water three times and separated from the aqueous layer. The resin was kept at 80 °C under a reduced pressure of 10 k Pa for 1 h to remove any unreacted aniline and/or formaldehyde.

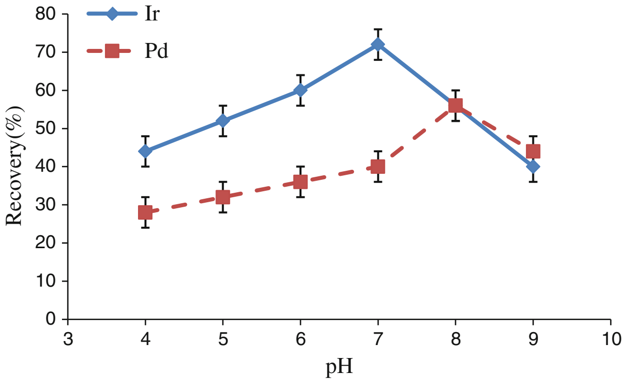

Fig. 2 Effect of pH on adsorption of Iridium and Palladium

MIP preparation

The chemical polymerization of aniline was performed as described in the literature (Kagaya et al. 2006; Karatepe et al. 2002; Sombra et al. 2001). However, in this work, Ammonium peroxide sulfate was used as the oxidizing agent. In a 150-mL reaction vessel, AFC was dissolved in optimum amount of 1 M HCl aqueous solution with various ratios. Then, 100 ppm of Ir(III) as a 20 mL liquid solution was added drop wise to the solution as a template; the same procedure was used for palladium. Then, 0.5 mL

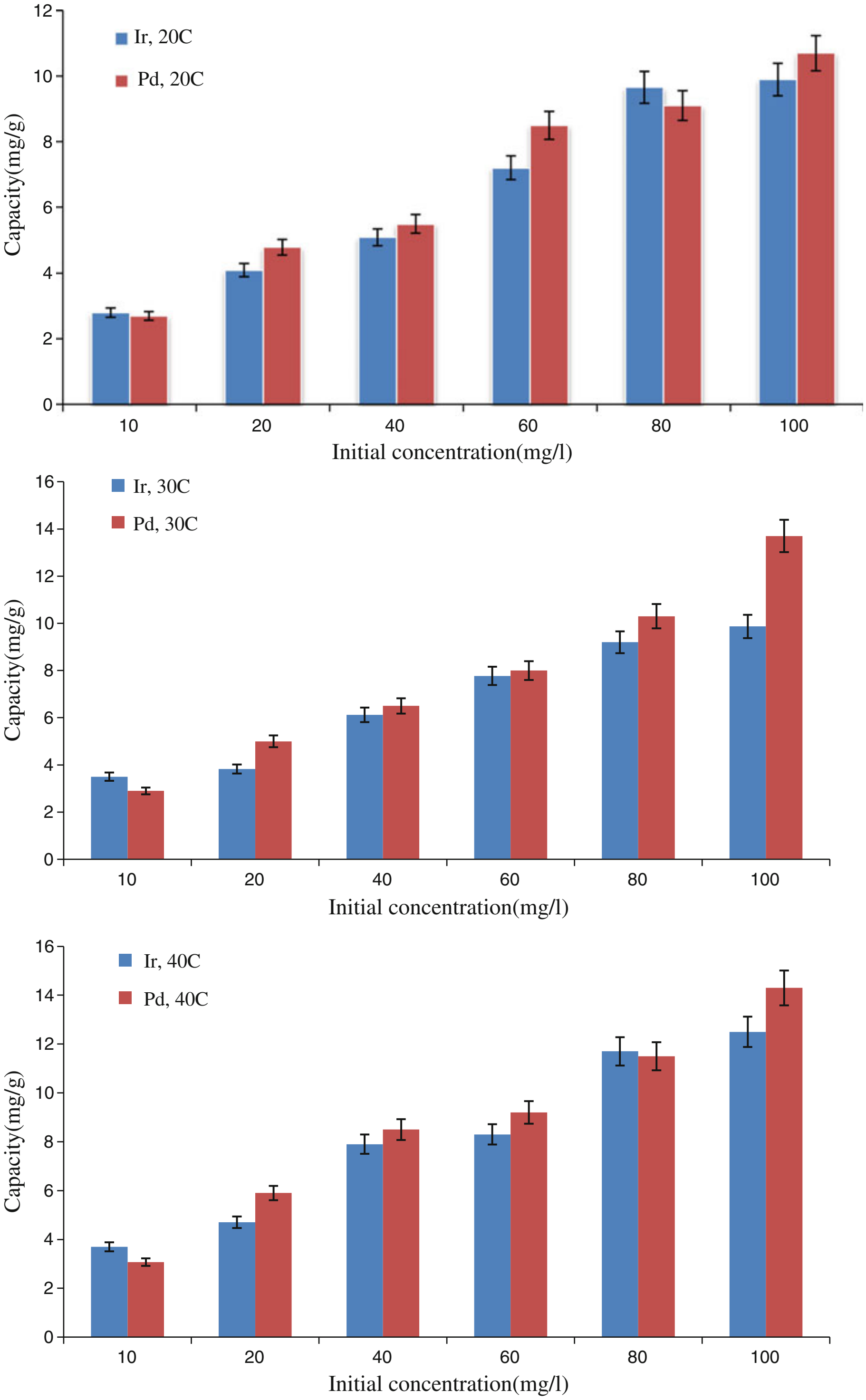

Fig. 3 The effect of initial concentration of Iridium and Palladium

of aniline was added to the solution as a cross-linker with vigorous stirring. After polymerization for 1 h at 25 °C, a dark polymer powder was obtained. The MIP was kept in the water bath at 0 °C for 2 h. The powder was washed with 0.5 M HNO3 to obtain MIP. The non-imprinted polymer (NIP) was prepared as the same protocol in the absence of the template ion.

The FT-IR spectra of IIP, Iridium and Palladium adsorbed onto IIP are shown in Fig. 1. As can be seen from Fig. 1, in all spectra, the adsorption band around 3,410 cm^{-1} reveals the stretching vibration of N–H group bonded with O–H group; 1,460 and 1,630 reveals stretching vibration of the (C = C) aromatic; 2,920 and 2,850 (C–H); and 1,041 (C–N).

Polymer through the amine groups was connected to the ion. The bands observed in the ion-imprinted aniline–formaldehyde at 3,410 and 1,630 cm^{-1} can be assigned to (NH$_2$) and aromatic ring shift to down for ion-imprinted aniline–formaldehyde loaded both ions and confirm the formation of ion-imprinted aniline–formaldehyde-Ir(III) complexes and also aniline–formaldehyde–Palladium complexes.

Results and discussion

Effect of initial pH on metal sorption

As the formation of metal ion complex and maximal efficiency for a given separation can be established by optimization of the pH, the parameter of pH is one of the most important factor affecting the adsorption of metal ions (Chen and Wang 2007). The effect of pH on the adsorption of Iridium and Palladium was studied individually by various pH values at the 0.3 μg mL^{-1} metal concentration. Their pH values were adjusted in range 4–9 with 0.01 M acetate or phosphate buffer solutions. Moreover, 0.1 g of resin was added to each solution and the mixture was shaken for 5 h. The results demonstrated in Fig. 2 which show the maximum adsorption capacity occurred at pH 7.0 for Iridium with maximum recovery 72 % and at pH 8.0 for Palladium with maximum recovery of 56 %. The degree of metal desorption with different eluting agents after Iridium and Palladium adsorption at optimum pH value was determined in batch experiments. Nitric acid at 0.5 M provided the best recovery for Ir with 88 % and for Pd with 75 % efficiencies.

Optimization of sorption time of Iridium and Palladium

Optimum sorption time of Iridium and Palladium ions obtained with this procedure that ion-imprinted aniline–formaldehyde (0.05 g) was shaken in parallel with two solutions (25 mL) with concentrations 0.3 mg/L of Iridium and Palladium ions for different times (10, 30, 45, 90, 180, 240 and 300 min) under optimum pH. After filtration of the sorbent, the concentrations of Iridium and Palladium ions in solution were determined with ICP-AES using the recommended batch method; however, less than 10 min shaking was required to reach the 11 % and 5.1 % sorption for Iridium and Palladium, respectively. The profile of Iridium and Palladium uptake on this sorbent reflects good accessibility of the chelating sites in the ion-imprinted aniline-formaldehyde.

Total sorption capacity

The 0.05 g of ion-imprinted aniline–formaldehyde resin beads were stirred for 4 h with 25 mL solution containing with 10–100 mg/L of Iridium and Palladium at the optimum pH and different temperatures of 20, 30 and 40 °C, respectively. The concentrations of metal ions in the supernatant liquid were estimated before and after the sorption by ICP. The sorption capacities of the resin for the ions were ascertained from the difference between the metal ions' concentrations in solution before and after the sorption. Fig. 3 indicates the effect of initial concentration of the Ir and Pd in the solution and the temperature during capacity sorption of Iridium and Palladium by ion-imprinted aniline–formaldehyde resin. The maximum adsorption capacity in initial concentration of 100 mg/L was found to be at 12.5 and 14.3 mg/g for Iridium and Palladium at the optimum pH and 40 °C.

Adsorption isotherm modeling and error analysis

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model which can be used for designing the adsorption systems. In this study, equilibrium data were analyzed by using the Langmuir (1916), Freundlich (1906), Redlich–Peterson

Table 1 Isotherms and their linear forms (with linear transformations of the Langmuir isotherm)

Isotherm		Linear form	Plot
Model	Equation		
Langmuir-1	$q_e = \frac{q_m K_a C_e}{1+K_e C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_a}$	$\frac{C_e}{q_e} vs. C_e$
Langmuir-2		$\frac{1}{q_e} = \frac{1}{q_m K_a} \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e} vs. \frac{1}{C_e}$
Langmuir-3		$q_e = q_m - \frac{1}{K_a} \frac{q_e}{C_e}$	$q_e vs. \frac{q_e}{C_e}$
Langmuir-4		$\frac{q_e}{C_e} = q_m K_a - k_a q_e$	$\frac{q_e}{C_e} vs. q_e$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$	$\ln(q_e) vs. \ln(C_e)$
Temkin	$q_e = \frac{RT}{b} \ln(A C_e)$	$q_e = B \ln A + b \ln C_e$	$q_e vs. \ln C_e$
Redlich–Peterson	$q_e = \frac{A C_e}{1+B C_e^g}$	$\ln(A \frac{C_e}{q_e} - 1) = g \ln(C_e) + \ln(B)$	$\ln(A \frac{C_e}{q_e} - 1) vs. \ln(C_e)$

(1959) and Temkin method (Ho and McKay 2000) which are the four most common isotherms of linear modeling (Table 1). However, the applied error functions which describe the distribution of a metal ion between a solid and a liquid phase and have been extensively used in the literature to model the uptake of various adsorbents (Mohanty et al. 2005; Mor et al. 2007; Das et al. 2002; Chandra and Garg 1992; Ho 2004). The constants of isotherm models can be evaluated from the intercepts and the slopes of their linear and nonlinear plots after bills from errors as defined in Table 2. For optimization, an error function for fitting of the isotherm equation on experimental equilibrium data is required (Ho

Table 2 Isotherms' parameters from best error function

Isotherm model	Method	Parameters	Ir (20C)	Ir (30C)	Ir (40C)	Pd (20C)	Pd (30C)	Pd (40C)
Langmuir-1	Linear	R^2	0.875	0.945	0.904	0.915	0.814	0.908
		q_m(mg/g)	13.92245	12.755	16.386	14.263	18.414	18.458
		K_a(L/mg)	0.025	0.034	0.030	0.027	0.021	0.027
		R_L	0.802	0.749	0.768	0.787	0.830	0.787
Langmuir-2	Linear	R^2	0.936	0.788	0.892	0.966	0.974	0.984
		q_m(mg/g)	9.756	8.881	11.467	12.012	13.454	17.322
		K_a(L/mg)	0.054	0.088	0.070	0.040	0.039	0.032
		R_L	0.651	0.531	0.589	0.716	0.721	0.760
Langmuir-3	Linear	R^2	0.689	0.618	0.677	0.780	0.674	0.890
		q_m(mg/g)	10.900	9.651	12.815	12.168	14.399	16.356
		K_a(L/mg)	0.044	0.076	0.058	0.040	0.035	0.036
		R_L	0.6928	0.568	0.635	0.716	0.741	0.736
Langmuir-4	Linear	R^2	0.689	0.617	0.677	0.780	0.673	0.890
		q_m(mg/g)	12.901	11.394	15.091	13.807	17.489	18.072
		K_a(L/mg)	0.031	0.048	0.039	0.030	0.024	0.029
		R_L	0.764	0.677	0.720	0.767	0.807	0.774
Langmuir	Nonlinear	R^2	0.923	0.931	0.923	0.937	0.906	0.928
		q_m(mg/g)	15.831	13.265	17.485	14.855	25.175	18.864
		K_a(L/mg)	0.0183	0.029	0.025	0.024	0.011	0.026
		R_L	0.845	0.775	0.800	0.806	0.901	0.794
Freundlich	Linear	R^2	0.964	0.946	0.962	0.961	0.965	0.958
		n	1.957	2.320	2.093	1.931	1.822	1.824
		K_f[(mg/g)(L/mg)]$^{1/n}$	0.981	1.385	1.427	1.024	1.024	1.187
Freundlich	Nonlinear	R^2	0.958	0.976	0.959	0.963	0.947	0.956
		n	1.795	2.109	1.944	1.908	1.564	1.871
		K_f[(mg/g)(L/mg)]$^{1/n}$	0.823	1.182	1.248	1.003	0.725	1.251
Temkin	Linear	R^2	0.787	0.860	0.827	0.824	0.735	0.822
		A(L/g)	1.0004	1.0004	1.0003	1.0004	1.0003	1.0003
		B(J/mol)	1.907	1.972	2.429	2.033	2.315	2.622
Temkin	Nonlinear	R^2	0.894	0.915	0.904	0.929	0.863	0.929
		A(L/g)	0.286	0.415	0.354	0.296	0.248	0.297
		B(J/mol)	2.878	2.582	3.375	3.030	3.727	3.918
Redlich–Peterson	Linear	R^2	0.961	0.966	0.967	0.954	0.946	0.941
		A(dm^3/g)	7.331	8.879	10.138	9.729	9.389	7.856
		B(dm^3/mg)^g	6.78536	5.890	6.474	8.966	8.862	6.046
		g	0.509	0.586	0.541	0.492	0.454	0.467
Redlich–Peterson	Nonlinear	R^2	0.957	0.975	0.959	0.963	0.946	0.956
		A(dm^3/g)	7.331	8.879	10.138	9.729	9.389	7.854
		B(dm^3/mg)^g	8.366	7.001	7.638	9.169	12.333	5.710
		g	0.454	0.539	0.496	0.486	0.368	0.483

Error function is the sum of square of the average squares of the errors (ERAV) $\sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_{\mathrm{exp}}-y_{\mathrm{cal}}\right)^2}$

et al. 2002; Rengaraj et al. 2007; Azam et al. 2010; Alihosseini et al.2010; Kailas et al. 2009). Moreover, ERRSQ, HYBRID, MPSD, ARE, EABS and ERAV (Gimbert et al. 2008) error functions were examined, and in each case, the isotherm coefficients were determined by minimization of error function in linear and nonlinear forms and also from the best error functions of isotherms parameters based on Tables 2 and 3.

Analogs to the Langmuir isotherm are important for the description of the binding sites for the drugs and enzyme catalysis. Simple linear regression will result in different parameter estimations (Kinniburgh 1986; Longhinotti et al. 1998). In addition, Langmuir types I, II, III and IV are used as more popular linear forms. The palladium obtained from Langmuir Type II (Table 2) is found as the best fit, because the correlation coefficient (R^2) from the result of fitted equation has the best error distribution (Kinniburgh 1986). In this isotherm, q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), and K_L is the Langmuir constant (L/mg). The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless constant separation factor or equilibrium, R_L, defined as (Kagaya et al. 2006; Ahalya et al. 2005):

$$R_L = 1/\left(1 + K_a \times C_0\right) \tag{1}$$

where K_a is the Langmuir constant and C_o is the initial concentration of the metal ions. The R_L value indicates the shape of the isotherm (Mckay et al. 1982) which between 0 and 1 indicate favorable absorption. From our study, Table 2 shows the values of R_L are in the range of 0–1 at optimum pH which confirms the favorable uptake of the palladium and Iridium.

Freundlich isotherm is an empirical equation employed to the described heterogeneous systems without lateral interactions, where K_F and $1/n$ are the Freundlich constants' characteristics of the system, indicating the maximum adsorption capacity and adsorption intensity, respectively, which are related to the affinity or binding strength (Davis et al. 2003).

Temkin isotherm model was chosen to evaluate the adsorption potentials of the adsorbent. The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers. In the linear form of Temkin equation (Table 1), $B = RT/b$ and b is the Temkin constant related to heat of sorption (J/mol). Moreover, A, R and T are the Temkin isotherm constant (L/g), the gas constant (8.314 J/mol K) and the absolute temperature (K), respectively.

Redlich–Peterson isotherm contains three constants (A, B, and g) and incorporates the features of the Langmuir and the Freundlich isotherms (Redlich and Peterson 1959). However, Iridium was obtained as the best fit in this work due to Redlich–Peterson model (Table2). The experimental data on the effect of an initial concentration of Iridium and Palladium on the ion-imprinted aniline–formaldehyde of the test medium were fitted to the isotherm models. Moreover, the graphical representations of these models are presented in Fig. 4, and all the constants are given in Table 2.

Adsorption thermodynamics

To study the nature of adsorption, the thermodynamic parameters for adsorption process, such as standard Gibbs, free energy change ($\Delta\ G^o$), the standard enthalpy change ($\Delta\ H^o$) and the entropy change's standard ($\Delta\ S^o$) were calculated with the following equations:

$$\Delta G = -RT\mathrm{Ln}(K) = \Delta H - T\Delta S \tag{2}$$

$$\mathrm{Ln}(K) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

Table 3 Thermodynamic parameters for the adsorption of Iridium and Palladium onto ion-imprinted aniline-formaldehyde at different temperatures

Thermodynamic parameters	Quantity						
C0 (mg/L)		10	20	40	60	80	100
ΔG° (KJ/mol) Iridium	T = 20 °C	−14.5	−13.6	−12.1	−12.0	−12.0	−11.4
	T = 30 °C	−15.9	−13.8	−13.1	−12.6	−12.3	−11.8
	T = 40 °C	−16.6	−14.9	−14.3	−13.2	−13.4	−12.9
ΔG° (KJ/mol) Palladium	T = 20 °C	−14.4	−14.0	−12.6	−12.4	−11.8	−11.7
	T = 30 °C	−15.2	−14.6	−13.3	−12.7	−12.6	−12.8
	T = 40 °C	−15.2	−14.6	−13.3	−12.7	−12.6	−12.8
ΔH° (KJ/mol) Iridium		15.8	5.8	19.8	6.2	8.3	9.9
ΔH° (KJ/mol) Palladium		6.9	10.7	20.0	2.6	10.2	12.7
ΔS° (J/mol K) Iridium		103.9	65.7	109.0	62.1	68.8	72.5
ΔS° (J/mol K) Palladium		72.7	84.0	110.3	50.9	75.3	83.5

$$K = \frac{X_S}{X_L} \tag{4}$$

$$K = \frac{\frac{M_S}{W}}{\frac{M_L}{M_W}} = \rho_w \frac{\frac{M_S}{W}}{\frac{M_L}{v}} = \frac{\rho_w * v}{W}\frac{M_S}{M_L} = \frac{\rho_w * v}{W}\frac{\frac{M_S}{v}}{\frac{M_L}{v}} = \frac{\rho_w * v}{W}\frac{C_0 - C_e}{C_e}$$
$$= \rho_w \frac{q_e}{C_e} \tag{5}$$

where K is the equilibrium constant, X_S is the mass fraction of cation in solid phase, X_L is the mass fraction of cation in liquid phase, M_S is the mass of cation in solid phase, M_L is the mass of cation in liquid phase, W is the mass of adsorbent, v is the volume of water in solution, ρ_W is the density of water, C_0 is the initial concentration of cation and C_e is the equilibrium concentration of cation. Additionally, the enthalpy change and entropy change values are calculated from the slope and intercept of the plot of ln (K) versus ($1/T$) (Fig. 5).

The thermodynamic parameters (ΔG°, ΔH° and ΔS°) of plots were used to compute the values (Table 3). Moreover, the experiments were carried out at 20, 30 and 40 °C. Due to the positive value of ΔH°, the adsorption process of

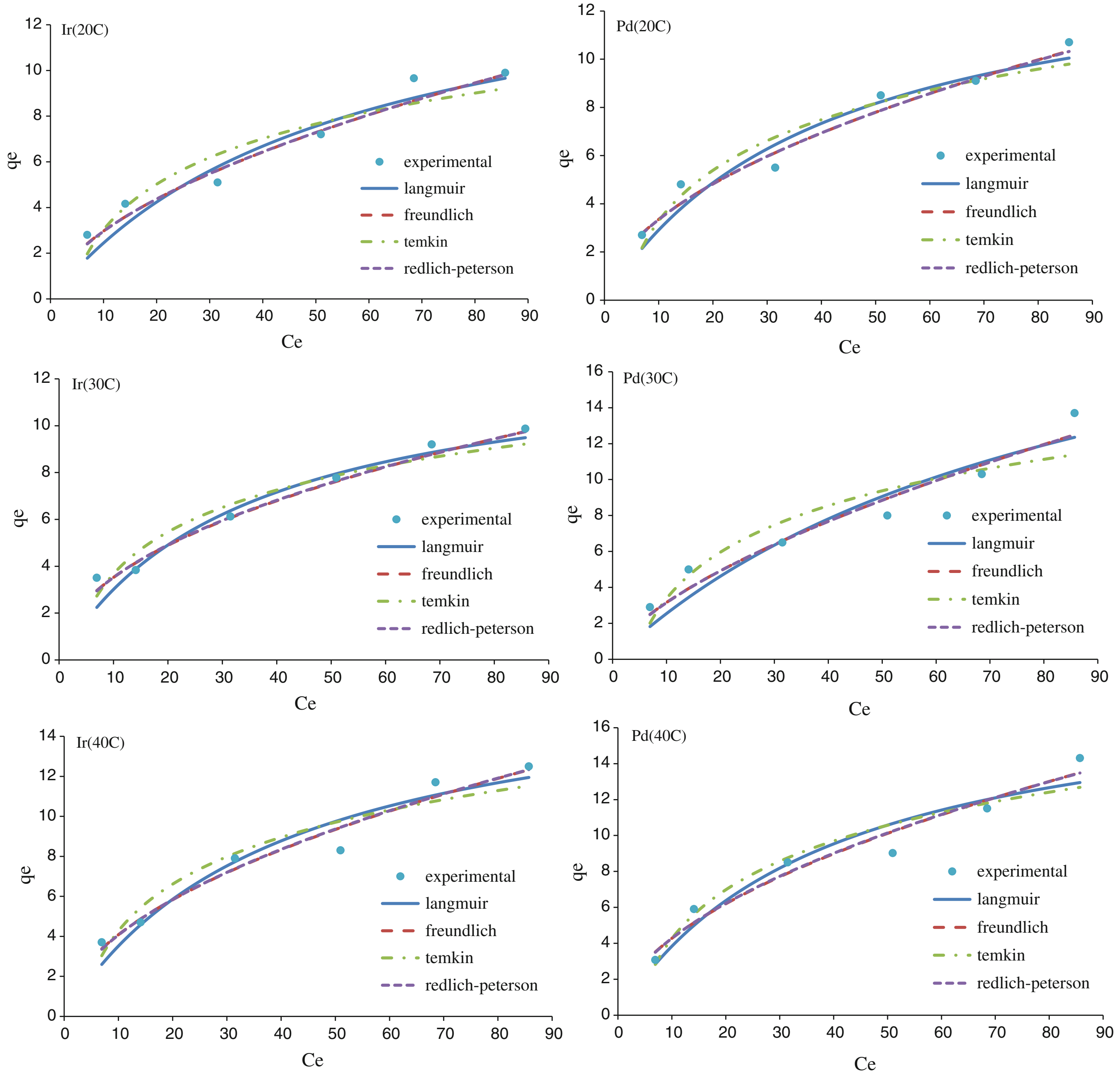

Fig. 4 Isotherms for the adsorption of Iridium and Palladium onto resin at various temperatures

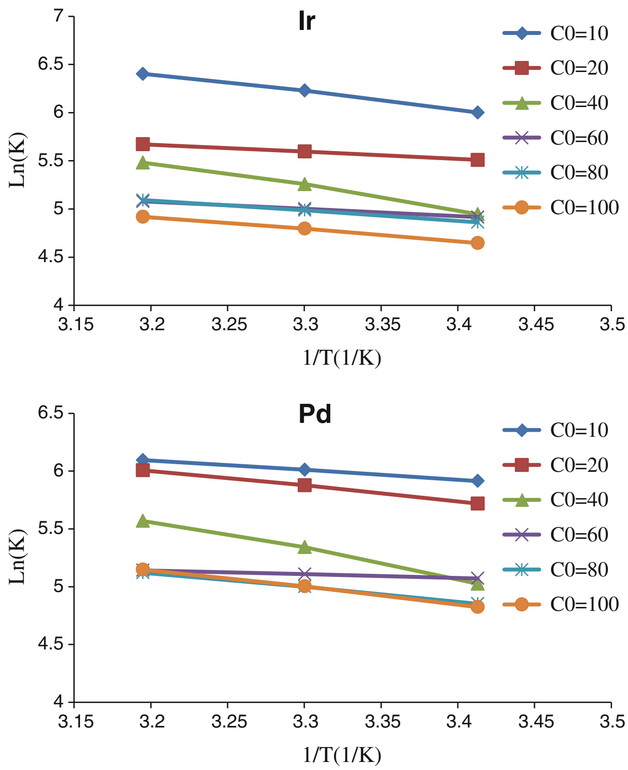

Fig. 5 Plot of ln *K* versus 1/*T* for the adsorption of Iridium and Palladium onto resin

Iridium and Palladium on ion-imprinted aniline–formaldehyde is endothermic. The Gibb's free energy value for all the systems is negative, and decrease in the value of $\Delta G°$ with increase in temperature shows the reaction occurs spontaneously, and it would be easier to occur at high temperature. It was reported that ΔG^{o} values up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while $\Delta G°$ values more negative than -40 kJ/mol involve charge sharing or transfer from the solid-phase surface to the metal ion to form a coordinate bond (chemical adsorption) (Horsfall et al. 2004). The $\Delta G°$ values were obtained in this study for the Ir^{3+} and Pd^{2+} ions are less than -17 kJ/mol which indicates physical adsorption was the predominant mechanism in the sorption process (Abdel Ghani and Elchaghaby 2007). The positive value of $\Delta S°$ suggests random growth at the solid/solution interface occurs in the internal structure of the adsorption of Iridium and Palladium onto ion-imprinted aniline–formaldehyde.

Effect of ion-imprinted and non-ion-imprinted on sorption of Iridium and Palladium

The sorption comparison of Iridium and Palladium on ion-imprinted aniline–formaldehyde and non-ion-imprinted aniline–formaldehyde was investigated (with each ion's concentration of 10 mg/L). The extraction percentage (*E* %) and the distribution ratio (*D*) was calculated from the following equations:

$$Q = (C_0 - C_e)\,V/W \tag{6}$$

$$E = (C_0 - C_e)\,/\,C_0 \tag{7}$$

$$D = Q\,/\,C_e \tag{8}$$

where Q represents the adsorption capacity (mg/g), C_0 and C_e represent the initial and equilibrium concentration of both ions (μg/mL), W is the mass sorbent (g), V is the volume of metal ion solution (L), E % is the extraction percentage and D is the distribution ratio (mL/g). The results in Table 4 show that the percentages of Iridium and Palladium sorption by ion-imprinted aniline-formaldehyde are 32.5 and 30.3 % higher than the non-ion-imprinted aniline–formaldehyde.

Analysis of real samples

Ion-imprinted aniline-formaldehyde resin was used to preconcentrate and determine Iridium and Palladium ions in tap water (Tehran). The pH of water sample was adjusted to optimize. Moreover, solid-phase extraction with ion-imprinted aniline-formaldehyde coupled with ICP-AES was applied for the determination of the Iridium and Palladium in water samples. None of the both ions were detected in the water samples (Table 5).

Table 4 Ion effects imprinted on sorption

Method	Amount of adsorbed Iridium (mg/L)	Amount of adsorbed Palladium (mg/L)	Extraction percentage Iridium	Extraction percentage Palladium	Distribution ratio Iridium	Distribution ratio Palladium
Ion imprinted	3.72	3.93	37.2	39.3	0.19	0.20
Non-ion imprinted	2.51	2.74	25.1	27.4	0.13	0.14

Table 5 Iridium and Palladium ion determination in water samples (I) and (II)

Analyze	Water sample I	Water sample II
Found (without spiking of Iridium and Palladium	N.D.	N.D.
Added Iridium (μg/mL)	0.2	0.4
Added Palladium (μg/mL)	0.2	0.4
Found Iridium, after pre-concentration (μg/mL)	1.85	3.80
Found Palladium, after pre-concentration (μg/mL)	1.88	3.85
Pre-concentration factor	10	10
Recovery (%)		
Ir	92.5	95
Pd	94	96.3
Standard deviation		
Ir	0.020	0.055
Pd	0.020	0.015
Relative standard deviation (%)[a]		
Ir	1.08	1.45
Pd	1.06	0.40

[a] For three determinations

Conclusion

A new ion-imprinted chelating sorbent is prepared by polymerizing the aniline–formaldehyde. The synthesis of the resin is simple and economical, and the resin has a good potential for tracing Iridium and Palladium from large volumes of samples. It also presents the advantage of high adsorption capacity, good reusability and high chemical stability. In addition, the sorption of the both ions from aqueous solutions was applied and shown in batch techniques. The different isotherms such as Freundlich, Langmuir, Temkin and Redlich–Peterson were examined to correlate with the experimental results by comparing theoretical plots of each isotherm with the experimental data for the adsorption of iridium and palladium ions on resin at 293°K. However,due to all results of these methods, the Langmuir Type II was found as the most fitted analytical data for palladium, whereas Redlich-Peterson was fitted for Iridium with maximum coefficient. Finally, with regard to the results of this study, it was concluded that pre-concentration by this sorbent combined with ICP-AES can be applied to trace Iridium and Palladium in water with satisfactory results.

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