

Pre-concentration and Determination of Platinum (IV) in Water Samples Using Chelating Resin by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Sid Kalal, H.^{1*}, Hoveidi, H.², Thagjof, M.¹, Pakizevand, N.¹, Almasian, M. R.¹
and Firoozzare, M. A.¹

¹Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, AEOI, P.O.Box 11365-3486, Tehran, Iran

²Graduate Faculty of Environment, University of Tehran, P.O. Box 14155-6135, Tehran, Iran

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ABSTRACT: A chelating resin is prepared by condensation polymerization of aniline with formaldehyde and characterized by FT-IR, elemental analysis and studied for the preconcentration and determination of trace Platinum ion from environmental water sample using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The optimum pH value for sorption of the metal ions was 5. The maximum adsorption capacities of resin (aniline- formaldehyde) were determined as 21.25, 14.72 and 11.9 mg/g at different temperatures 20, 30 and 40 °C, respectively. The best desorption of the metal ions from resin was obtained by 0.5 mol/L nitric acid as eluting agent. The profile of Platinum uptake on this sorbent reflects good accessibility of the chelating sites in the aniline-formaldehyde. The equilibrium adsorption data of Platinum ion modified resin were analyzed by four isotherm models such as Langmuir, Freundlich, Temkin and Redlich–Peterson. Langmuir isotherm parameters obtained from the four Langmuir linear equations by using linear method, Langmuir-1 is the most popular linear form, and it had the highest coefficient of determination compared with the other Langmuir linear equations. 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 Pt (IV) ion was spontaneous nature and exothermic. The method was applied for Platinum ions determination from tap water sample.

Key words: Solid phase, Extraction, Environment, Platinum, Isotherm

INTRODUCTION

Platinum, which is a silvery-white metal, is the most common and widely used of all the platinum group metals (PGMs) (Jonck, 2008, Vlasánková and Sommer, 1999). It is also used in many anti-pollution devices, most notable is the catalytic converter, and has been given the nick name the “Environmental Metal” (Amethyst Galleries, Inc, 2011). A remarkable variety of methods have been considered for determination of metals concentration (Bhakta and Munkage, 2011, Dekhil *et al.*, 2011, Li *et al.*, 2011, Bagheri Sadeghi *et al.*, 2011, Yu *et al.*, 2011, Naim *et al.*, 2011, Chen *et al.*, 2011, Mane and Bhosle, 2012, Kargar *et al.*, 2012), however, the direct determination of these elements like platinum in real samples is a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in those samples, which are often below the detection

limits of available techniques (Camel, 2003, Lemos *et al.*, 2006). To solve this problem, pre-concentration–separation procedures have been proposed. Pre-concentration is a very important issue for achievement of low detection limits (Prabhakaran and Subramanian, 2003, Amran *et al.*, 2011, Dhir, *et al.*, 2010, Salim and Munkage, 2009). There are many methods of pre-concentration and separation such as liquid–liquid extraction (Saito, *et al.*, 2000) and ion exchange techniques (Alguacil, *et al.*, 2005, Hubicki, *et al.*, 2008). Trace platinum can be retained on the surface of aniline-formaldehyde and then desorbed with HNO₃ 0.5 mol/L prior to determination by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In this study, the linear least-squares method and a non-linear method of four widely used isotherms (Yuh-Shan, 2006), the Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Redlich-Peterson Peterson

*Corresponding author E-mail: hsidkalal@aeoi.org.ir

(Redlich and Peterson, 1959) and Temkin (Ho and McKay, 2000) were compared in an experiment examining platinum ion sorption onto aniline-formaldehyde.

MATERIALS & METHODS

ICP-AES Varian, Vista-pro (Salt lake city, Australia) was used for measuring the concentration of platinum ion. The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland) by the potassium bromide pellet method. Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. HCl, H₂SO₄, HNO₃, NaOH, NaCl, CH₃COOH, CH₃COONa, NaH₂PO₄, Na₂HPO₄, Pb(NO₃)₂, CuSO₄·5H₂O, Co(NO₃)₂·6H₂O, Ni SO₄·6H₂O, Zn SO₄·7H₂O, ethylenediaminetetraacetic acid (EDTA), CH₃COCH₃, C₂H₅OH, NH₃, Pt (IV), aniline and formaldehyde were products of Merck (Darmstadt, Germany). All the solutions were prepared in deionized water using analytical grade reagents. The stock solution (500 mg/L) of Pt (IV), were prepared from standard Platinum solution (1000 mg/L). 10 mL of 0.1 mol/L acetate buffer (pH= 3 – 6.5) and 0.01 mol/L phosphate buffer (pH= 6.5 - 9) were used to adjust the pH of the solutions, wherever suitable. A mixture of 15 mL aniline and 15 mL formaldehyde was acidified with drop wise adding concentrated HCl. The mixture was blended till formation of a solid polymer. The polymer (aniline- formaldehyde) was grinded and washed with warm water and acetone several times. The resin was dried at 60 °C and placed in a desiccator. The structural formula of synthesized resin is given in Fig. 1. The synthesized polymer was characterized by IR and elemental analyses. An IR spectrum of this chelating resin was run to verify the structure of aniline-formaldehyde: 1508 (Aromatic C=C) and 1696 (N=N) cm⁻¹. The elemental analysis for aniline- formaldehyde (found: C, 75.26, H, 5.93, N, 12.37 %, calculated for C₇NH₇: C, 80.00, H, 6.6, N, 13.3 %) confirm formation of the polymer. A sample solution (50 mL) containing (0.3 µg/mL) of Pt (IV) was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. The 0.05 g of aniline- formaldehyde was added to the bottle and

the mixture was shaken for optimum time. The resin was filtered and sorbed metal ions were eluted with 0.5 M HNO₃ (10 mL). The concentration of metal ions in the eluant was determined by ICP-AES. The wavelength of 214.423 nm was used for Platinum determination. Isotherm studies were carried out by adding a fixed amount of adsorbent (0.2 g) to a series of beakers filled with 50 ml diluted solutions of Platinum (IV) (10-80 µg/mL). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4 h) at 20°C, 30 and 40°C and optimum pH (5). pH adjustments have been done using 0.01 mol L⁻¹ acetate buffer. The beakers were then removed from the shaker, and the final concentration of Platinum in the solution was measured by ICP-AES. The amount of Pt (IV) at equilibrium q_e (mg/g) onto aniline-formaldehyde was calculated from the following equation:

$$q_e = (C_0 - C_e) V/w \quad (1)$$

where C₀ and C_e (mg/L) are the liquid phase concentrations of Pt (IV) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

RESULTS & DISCUSSION

The degree metal desorption at optimum pH values was determined by batch equilibration technique. Among of ethylenediaminetetraacetic acid (EDTA) 0.1 mol/L, H₂SO₄ 0.5 mol/L, and HNO₃ 0.5 mol/L as the elution agent, it was observed the HNO₃ 0.5 mol/L provided the best recovery. The degree metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (the volume of each 50 mL) containing 2.5 mg/L of Platinum was taken. Their pH values were adjusted in range 3-9 with 0.01 M acetate and/or phosphate buffer solutions. 0.05 g of aniline- formaldehyde was added to each solution and the mixture was shaken for 4 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Platinum content (by ICP-AES) in supernatant liquid and in the eluate obtained by desorbing the metal ion from aniline-formaldehyde with 0.5 M nitric acid (10 mL). The

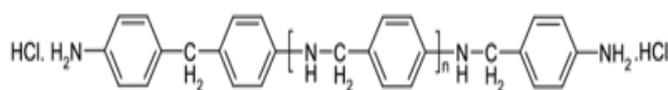


Fig.1. Formula of chelating resin (aniline- formaldehyde)

optimum pH range for the sorption of the metal ion is shown in Fig. 2. The maximum recovery was 76% at pH 5. The 0.05 g of resin beads were stirred for 4 h. with 25 mL solution containing 10-80 mg/L of Platinum, at optimum pH and different temperatures 20, 30 and 40 °C. The metal ion concentration in the supernatant liquid was estimated by ICP. The sorption capacity of the resin for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. Fig. 3 indicates the effect of initial concentration of the Pt in the solution and the temperature on capacity sorption of Pt (IV) by aniline-formaldehyde resin. The adsorption capacity in initial concentration of 80 mg/L of Pt (IV) at optimum pH and 20 °C was obtained 21.25 mg/g.

The Platinum was sorbed and desorbed on 0.05 g of the aniline- formaldehyde several times. It was found that sorption capacity of resin after 10 cycles of its equilibration with Platinum ion, changes less than 5 %. Therefore, repeated use of the resin is feasible. The resin cartridge after loaded with samples can be readily regenerated with 0.5 mol/L HNO₃. The sorption capacity of the resin stored for more than 6 month under ambient conditions has been found to be practically unchanged. Optimum sorption time of Platinum ions obtained with this procedure that aniline-formaldehyde (0.05 g) was shaken with 50 mL of solution containing 0.3 mg/L of Platinum for different times (10, 30, 45, 90, 180,240 and 300 min) under optimum pH. After filtration of the sorbent, the

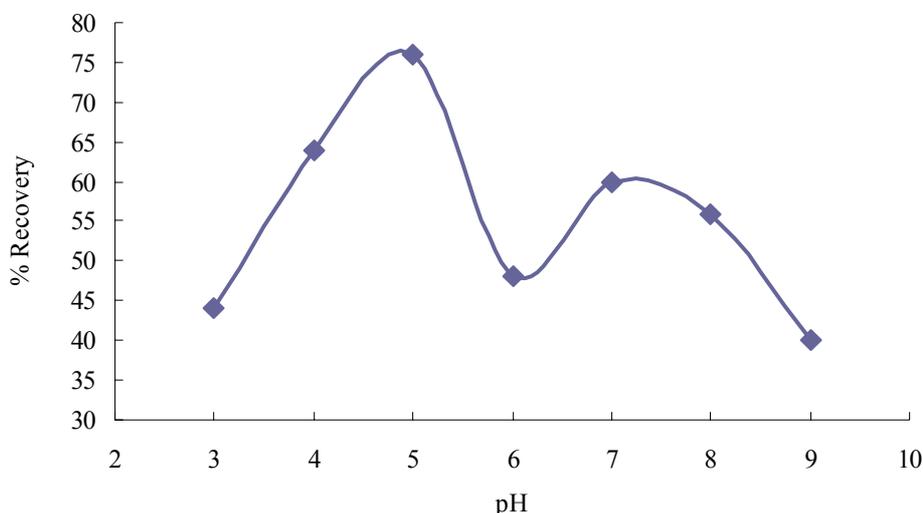


Fig. 2. Effect of pH sorption of Pt (VI), onto aniline-formaldehyde

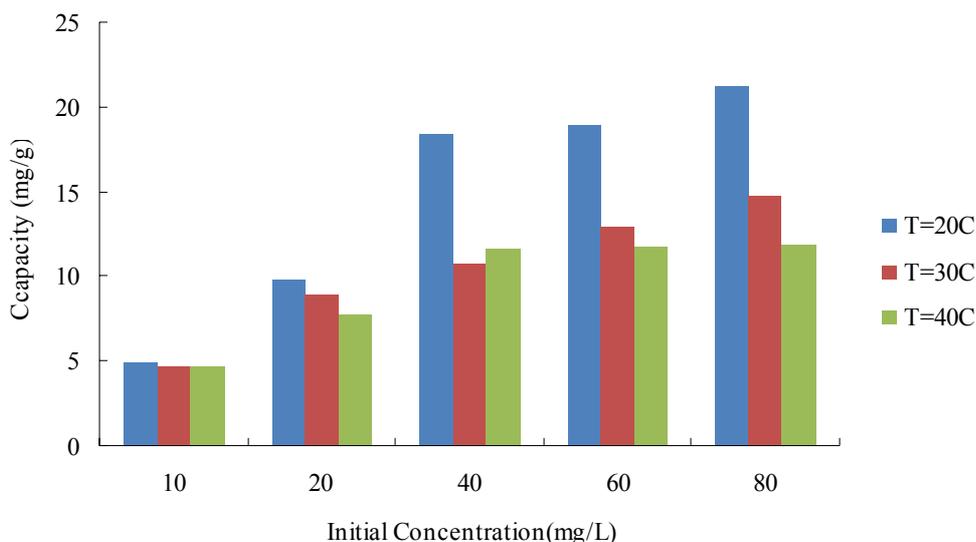


Fig. 3. Effect of initial concentration of the Pt (IV) and the temperatures on capacity sorption of Pt (IV) onto aniline-formaldehyde resin

concentration of Platinum ions in solution was determined with ICP-AES using the recommended batch method. The sorption as a function of contact time for all the metal ions is shown in Fig.4. Less than 10 min shaking was required for 34.75 % sorption. The profile of Platinum uptake on this sorbent reflects good accessibility of the chelating sites in the aniline-formaldehyde.

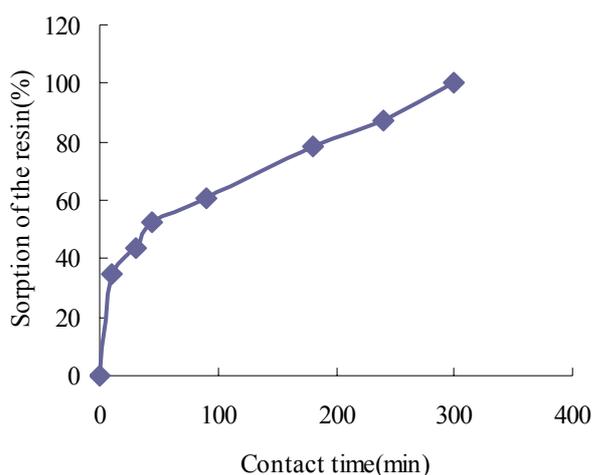


Fig. 4. Kinetics of Pt (VI), sorption on aniline-formaldehyde resin

The Langmuir(Langmuir, 1916), Freundlich (Freundlich, 1906), Redlich-Peterson (Redlich and Peterson, 1959) and Temkin (Ho and McKay, 2000) are the four most common isotherms linear (Table 2 and Figs 5 to 8). The constants of isotherm models can be evaluated from the intercepts and the slopes of the linear and non linear (Table 3 and Fig. 11) plots of them, after considering the errors as defined in Tables 2, 3. The Langmuir (four different types) equation was given in the following form (Langmuir, 1918):

$$q_e = q_{max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (2)$$

where 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 equation (2) can be rearranged to a linear form:

$$C_e/q_e = (1/q_{max} \cdot K_L) + (C_e/q_{max}) \quad (3)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e for

Langmuir 1 fig.5, the linear plots of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ for

Langmuir 2 fig.6. the linear plots of q_e versus $\frac{q_e}{C_e}$ for

Langmuir 3 fig.7 and the linear plots of $\frac{q_e}{C_e}$ versus

q_e for Langmuir 4 fig. 8.

Conformation of the experimental data in to Langmuir (four different types) isotherms models indicates the homogeneous nature of aniline-formaldehyde surface. Langmuir parameters calculated from Equation (3) are listed in Table 2.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L , defined as (Hall *et al.*, 1966):

$$R_L = 1 / (1 + K_L \cdot C_0) \quad (4)$$

Table 1 shows the values of R_L are in the range of 0-1 at optimum pH which confirms the favorable uptake of the Pt (IV).

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written as (Freundlich, 1906):

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant (mg/g) (L/mg)^{1/n} and $1/n$ is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the Equation (5):

$$\ln(q_e) = \ln(K_F) + 1/n \ln(C_e) \quad (6)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ (Fig. 9) enables the constant K_F and exponent $1/n$ to be determined. The Freundlich equation predicts that the Pt (IV) concentration on the adsorbent will increase as long as there is an increased in the Pt (IV) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (7)$$

Table1. Effect of eluant on desorption of Platinum (IV) ion

Eluant	0.1M EDTA	0.5M H ₂ SO ₄	0.5M HNO ₃
Recovery	53%	71%	92%

Table 2. Isotherm parameters obtained using the linear method

Freundlich Linear isotherm model				
Temperature	$K_F (mg/g)(L/mg)^{1/n}$	n	R^2	
20 °C	10.30	4.38	0.8638	
30 °C	6.05	4.49	0.9075	
40 °C	5.53	4.66	0.9484	
Langmuir Linear 1 isotherm model				
Temperature	$q_{max}(mg/g)$	$K_L (L/mg)$	R_L	R^2
20 °C	20.48	1.54	0.0608	0.9962
30 °C	13.39	0.34	0.2266	0.9825
40 °C	12.05	0.70	0.1253	0.9991
Langmuir Linear 2 isotherm model				
Temperature	$q_{max}(mg/g)$	$K_L (L/mg)$	R_L	R^2
20 °C	19.65	2.80	0.0345	0.9974
30 °C	13.14	0.91	0.0994	0.9813
40 °C	11.18	1.22	0.0756	0.9462
Langmuir Linear 3 isotherm model				
Temperature	$q_{max}(mg/g)$	$K_L (L/mg)$	R_L	R^2
20 °C	20.34	2.59	0.0371	0.9830
30 °C	13.30	0.90	0.1001	0.8889
40 °C	11.59	1.10	0.0834	0.8851
Langmuir Linear 4 isotherm model				
Temperature	$q_{max}(mg/g)$	$K_L (L/mg)$	R_L	R^2
20 °C	20.44	2.55	0.0378	0.9830
30 °C	13.67	0.80	0.1115	0.8889
40 °C	11.92	0.94	0.0960	0.8551

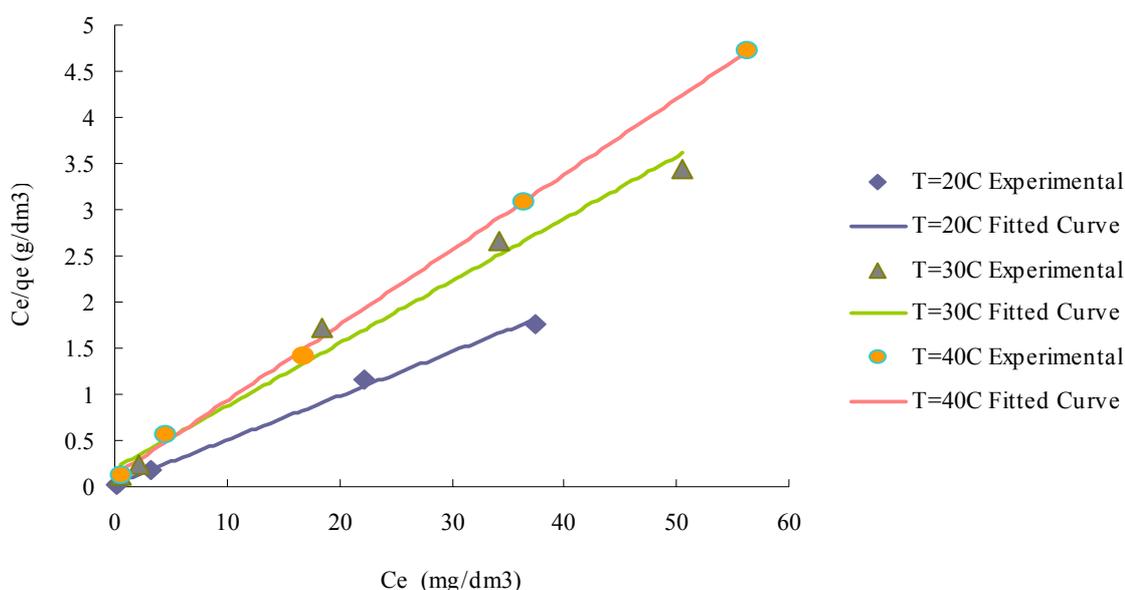


Fig. 5. Langmuir-1 isotherm obtained using the linear method for the sorption of Pt (IV) onto aniline-formaldehyde at various temperatures

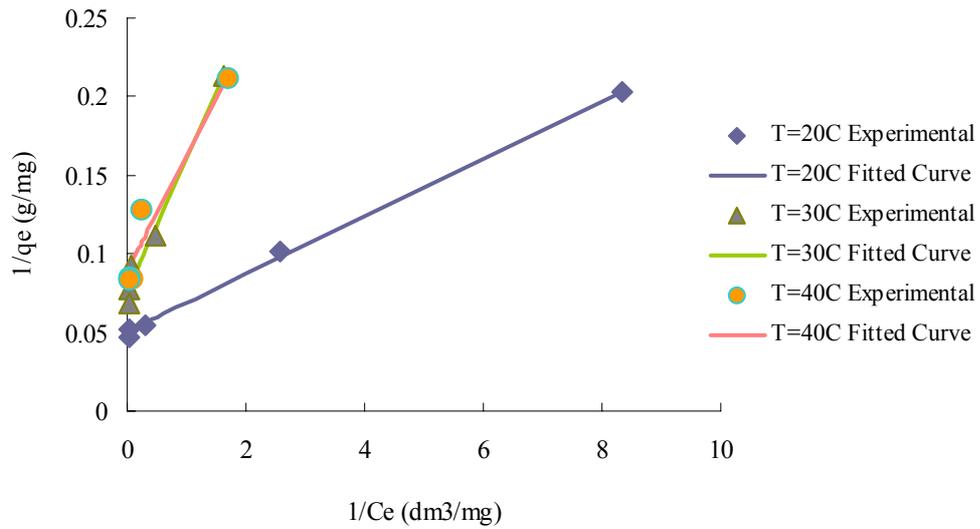


Fig. 6. Langmuir-2 isotherm obtained using the linear method for the sorption of Pt (IV) onto aniline-formaldehyde at various temperatures

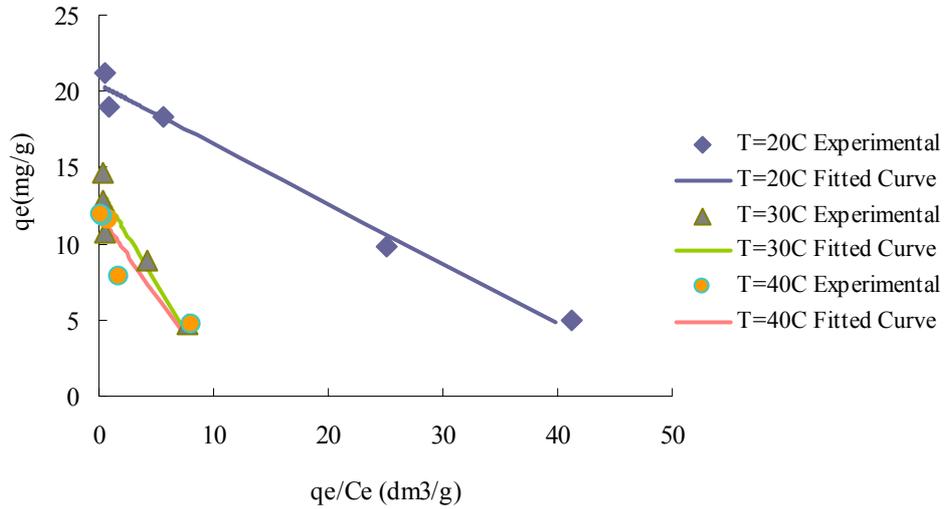


Fig.7. Langmuir-3 isotherm obtained using the linear method for the sorption of Pt (IV) onto aniline-formaldehyde at various temperatures

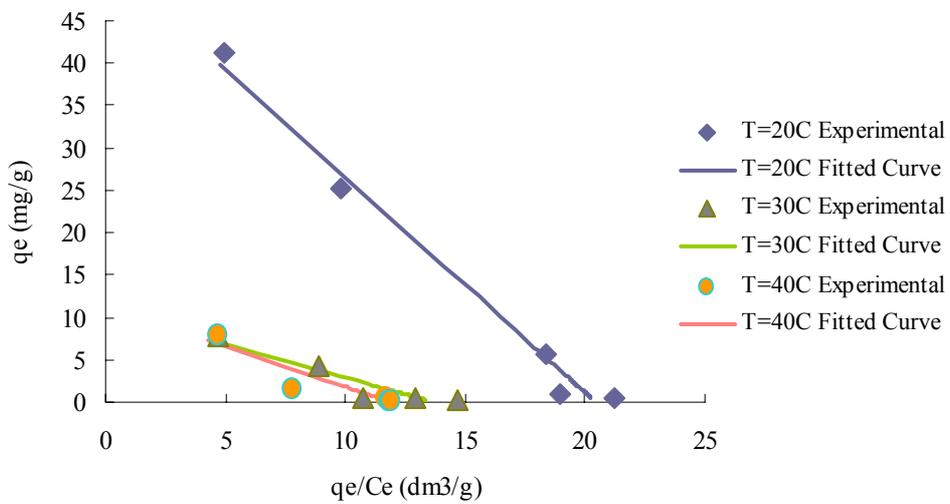


Fig. 8. Langmuir-4 isotherm obtained using the linear method for the sorption of Pt (IV) onto aniline-formaldehyde at various temperatures

Table 3. Isotherm parameters obtained using the non-linear method

Langmuir isotherm model				
Temperature	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
20 °C	20.48	2.46	0.039	0.9877
30 °C	13.39	0.86	0.104	0.8984
40 °C	12.05	0.75	0.117	0.9156
Freundlich isotherm model				
Temperature	K_F (mg/g)(L/mg) ^{1/n}	n		R^2
20 °C	11.54	5.62		0.8566
30 °C	6.31	4.82		0.9295
40 °C	5.97	5.29		0.9121
Temkin isotherm model				
Temperature	A (L/g)	B (J/mol)	b(J/mol)	R^2
20 °C	88.96	2.69	905.58	0.9257
30 °C	24.03	1.96	1285.28	0.9362
40 °C	27.99	1.71	1521.80	0.9493
Redlich–Peterson isotherm model				
Temperature	g	B (dm ³ /mg) ^g	A (dm ³ /g)	R^2
20 °C	0.99	2.65	52.56	0.9881
30 °C	0.85	3.91	30.86	0.9419
40 °C	0.90	2.12	17.62	0.9518

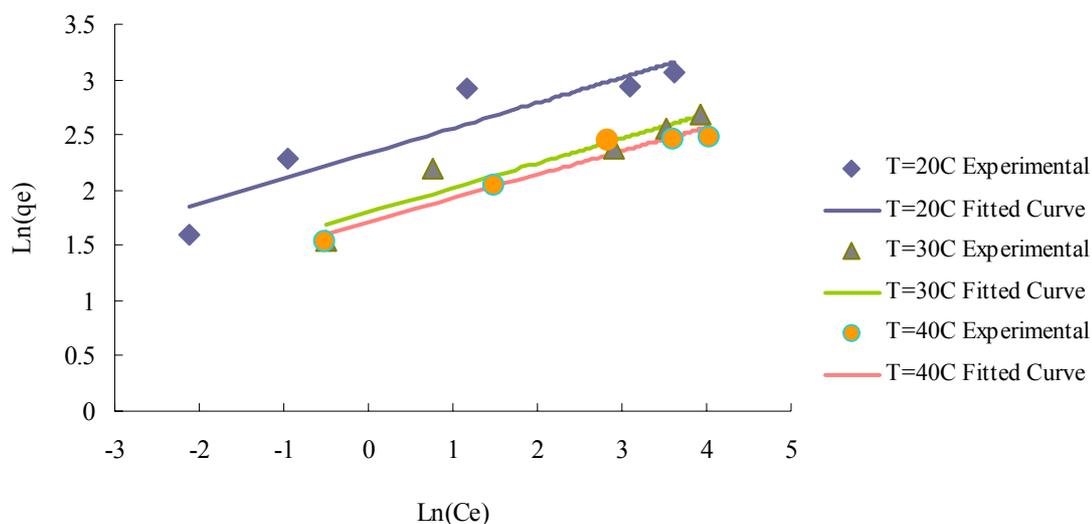


Fig. 9. Freundlich isotherm for Pt (IV) adsorption onto aniline-formaldehyde at various temperatures

Platinum (IV) in Water Samples

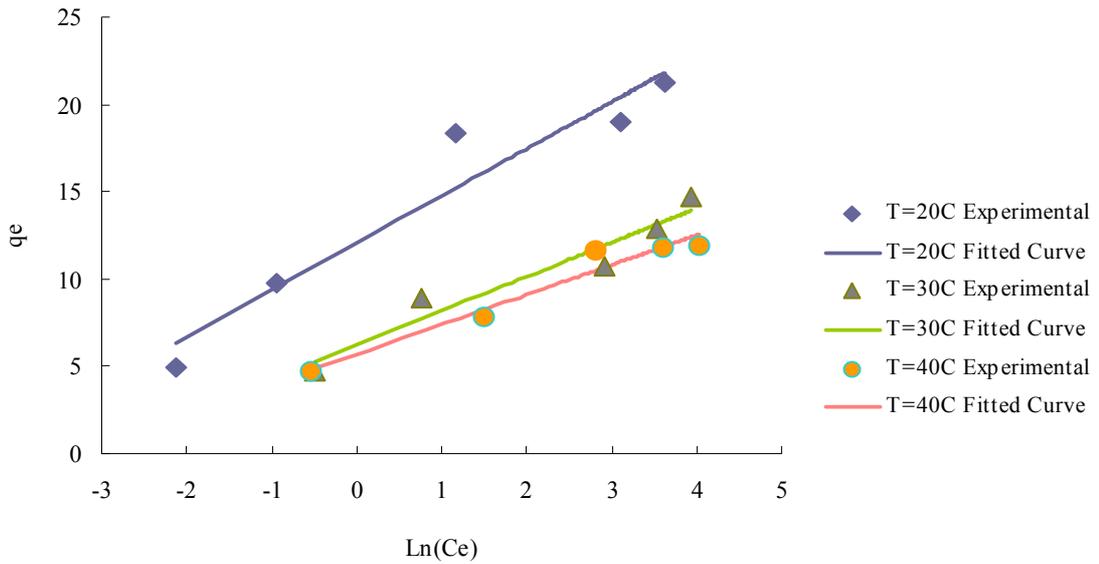


Fig. 10. Temkin isotherm for Pt (VI) adsorption onto aniline-formaldehyde at various temperatures

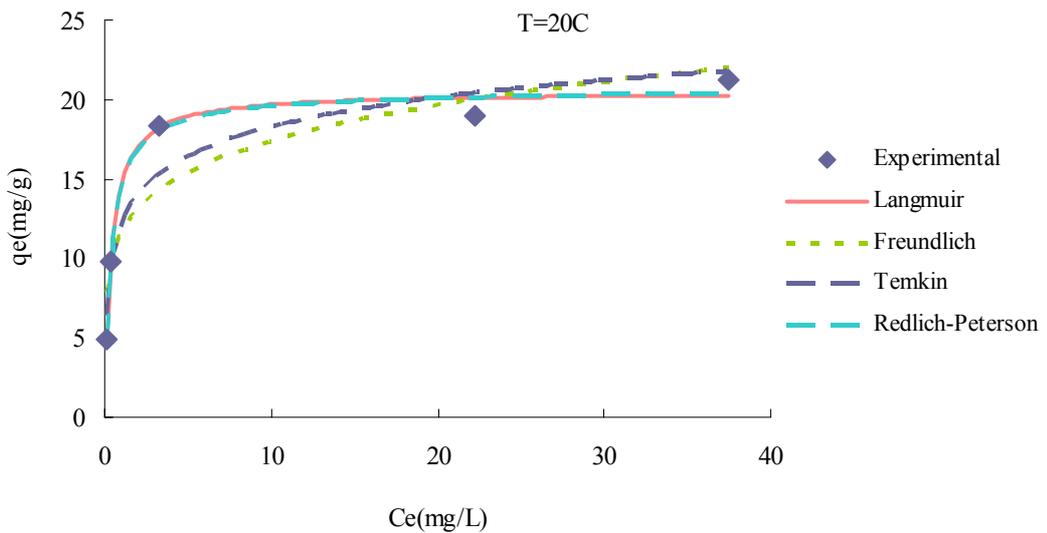


Fig.11. Isotherms obtained using the non-linear method for the sorption of Pt (IV) onto aniline-formaldehyde at a temperature of 20°C

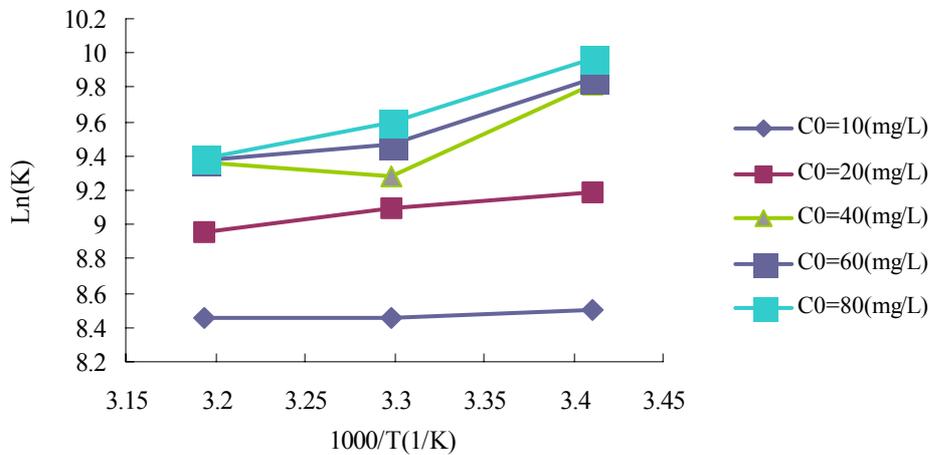


Fig. 12. Plot of ln K vs. 1/T for the adsorption of Pt (IV) on aniline-formaldehyde

and can be linearized:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

Where $B=RT/b$ and b is the Temkin constant related to heat of sorption (J/mol). A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T is the absolute temperature (K). Therefore plotting q_e versus $\ln C_e$ (Fig.10) enables one to determine the constants A and B . Temkin parameters calculated from Equation (7 and 8) are listed in Table 1. The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$), which characterize the isotherm. The limiting behavior can be summarized as follows:

Where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (10)$$

i.e. the Langmuir form results.

Where constants A and B are much greater than unity (Ho and Ofomaja, 2006):

$$q_e = (A/B)C_e^{1-g} \quad (11)$$

i.e. the Freundlich form results.

Where $g = 0$

$$q_e = (A/B)C_e \quad (12)$$

i.e. the Henry's Law form results.

Eq. (9) can be converted to a linear form by taking logarithms:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \quad (13)$$

Three isotherm constants, A , B , and g can be evaluated from the linear plot represented by Eq. (13) using a trial and error procedure, which is applicable to computer

operation. It was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination, R^2 , for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln[A(C_e/q_e)^{-1}]$ and to obtain the best value of A which yields a maximum 'optimized' value of R^2 using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

To study the nature of adsorption, the thermodynamic parameters for adsorption process, such as the standard Gibbs free energy change (ΔG°), the standard enthalpy change (ΔH°), and the standard entropy change (ΔS°), were calculated with the following equations:

$$\Delta G^\circ = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

$$\ln(K) = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

$$K = \frac{X_s}{X_L}$$

$$K = \frac{\frac{M_s}{W}}{\frac{M_L}{m_w}} = \rho_w \frac{\frac{M_s}{W}}{\frac{M_L}{v}} =$$

$$\frac{\rho_w v}{W} \frac{M_s}{M_L} = \frac{\rho_w v}{W} \frac{\frac{M_s}{v}}{\frac{M_L}{v}} =$$

$$\frac{\rho_w v}{W} \frac{C_0 - C_e}{C_e} = \rho_w \frac{q_e}{C_e}$$

where K is the equilibrium constant, X_s is mass Fraction of cation in Solid Phase, X_L is mass fraction of cation in liquid Phase, M_s is Mass of cation in solid Phase, M_L is mass of cation in liquid Phase, W is mass of adsorbent, v is volume of water in solution, ρ_w is density of water, C_0 is Initial concentration of cation, C_e is equilibrium concentration of cation.

The values of enthalpy change and entropy change are calculated from the slope and intercept of the plot of $\ln(K)$ versus $(1/T)$. (Fig. 12).

The thermodynamic parameter, ΔG° , ΔH° and ΔS° is shown in Table 4. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for Pt (IV) to sorption onto aniline-formaldehyde. The value of ΔH° was negative, indicating that the sorption reaction is exothermic. The positive value of ΔS° shows the

increasing randomness at the solid/liquid interface during the sorption of platinum ions onto aniline-formaldehyde.

In order to evaluate the selectivity of the chelating resin, the effect of some metal ions (20 mg/L) on the sorption behavior of Pt ion (concentration 20 mg/L) was investigated. The extraction percentage (E %), was calculated from the following equations:

$$Q = (C_0 - C_e) V / W \quad (16)$$

$$E = C_e / C_0 \quad (17)$$

$$D = E V / W \quad (18)$$

$$L = C_e^{No-ion} - C_e / C_e^{No-ion} \quad (19)$$

Where Q represents the adsorption capacity (mg/g), C_0 and C_e represent the initial and equilibrium concentration of Pt ion ($\mu\text{g/mL}$), W is the mass sorbent

(g), V is the volume of metal ion solution (L) and E % is the extraction percentage. The result was shown in Table 5. It indicates that the most effective ions on adsorption of Pt ion on aniline- formaldehyde. The effects of the other mentioned foreign ions at given concentrations are negligible. The adsorption of Pt ion on the aniline- formaldehyde in presence of all mentioned ions (with the concentration of 20 mg/L for each ion) shows that the Pt ion can be determined quantitatively in the environmental samples.

Aniline- formaldehyde was used to preconcentrate and determine Platinum ions in tap water Tehran , Iran. The pH of water sample was adjusted to the optimum pH 5. Solid phase extraction with aniline- formaldehyde coupled with ICP-AES was applied to determination of Platinum in water sample. No Platinum ion was detected in the water sample, these results demonstrate the applicability of the procedure for Platinum determination in samples with high recovery (>68%)(Table 6).

Table 4. Thermodynamic parameters of Pt (IV) adsorption on aniline-formaldehyde

Thermodynamic parameters		Quantity				
C_0 [mg/L]		10	20	40	60	80
ΔG [KJ/mol]	T=20C	-20.7	-22.4	-23.9	-24.0	-24.3
	T=30C	-21.3	-22.9	-23.4	-23.9	-24.2
	T=40C	-22.0	-23.3	-24.4	-24.4	-24.4
ΔH [KJ/mol]		-1.8	-8.7	-17.5	-18.3	-22.2
ΔS [J/mol.K]		64.4	46.7	21.1	19.2	7.0

Table 5. Effect of other ions on sorption

Interfering	A	L (%)	E (%)	D
-----	6.1	0	30.5	152.5
Ni (II)	2.26	62.95	11.3	56.5
Co (II)	3.25	46.72	16.25	81.25
Zn (II)	2.38	60.98	11.9	59.5
Cd (II)	1.7	72.13	8.5	42.5
Fe(II)	3.4	44.26	17.0	85.0
Cu (II)	2.08	65.90	10.4	52.0
Mixed above ion	1.5	75.41	7.5	37.5

A: Amount of adsorbed Pt (IV) ($\mu\text{g/mL}$), L: Loss adsorption (%), E: extraction percentage (%) and D: distribution ratio

Table.6. Results obtained for Pt ion determination in water sample: (I), (II) and (III)

Analyte	(I)	(II)	(III)
Sample (without spiking of Pt (IV))	N.D.	N.D.	N.D.
Added Pt (IV) ($\mu\text{g/mL}$)	0.4	0.6	0.8
Found Pt (IV), after pre concentration ($\mu\text{g/mL}$)	2.43	4.1	5.1
Preconcentration factor	10	10	10
Recovery %	60.75	68.33	63.75
Standard deviation	0.021	0.135	0.236
Relative standard deviation (%) ^a	0.86	3.31	4.62

a: For three determinations

CONCLUSION

A new chelating resin shows higher adsorption selectivity for Platinum ions, and adsorbed ions can be readily desorbed from the resin by 10 mL of 0.5 mol/L HNO₃. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Platinum from large sample volumes. The resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. The R_L values showed that the aniline-formaldehyde was favorable for the adsorption of Platinum. The Langmuir isotherm parameters obtained from the four Langmuir linear equations using the linear method. Langmuir-1 is the most popular linear form, and it had the highest coefficient of determination compared with the other Langmuir linear equations. Thermodynamic parameters shows that the sorption of Platinum onto aniline-formaldehyde is spontaneous nature and exothermic. Preconcentration by this resin combined with ICP-AES can be applied to the determination of trace Platinum ions in water and the mineral reference sample with satisfactory results.

REFERENCES

- Ahalya, N., Kanamadi, R. D. and Ramachandra, T. V. (2005). Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*). *Electronic J. Biotechnol.*, **8** (3), 258-264.
- Alguacil, F. J., Adeva, P. and Alonso, M. (2005). Processing of Residual Gold (III) Solutions via Ion Exchange. *Gold Bull.*, **38**, 9-13.
- Amethyst Galleries, Inc. (2011). <http://www.galleries.com/Platinum>.
- Amran, M. B., Panggabean, A. S., Sulaeman, A. and Rusnadi, M. (2011). Preparation of a Chelating Resin and its Application as a Preconcentration System for Determination of Cadmium in River Water by Flow Injection Analysis. *Int. J. Environ. Res.*, **5** (2), 531-536.
- Bagheri Sadeghi, H., Sid Kalal, H., Hoveidi, H., Molavi, Z. and Adeli Asl, N. (2011).
- A New Potentiometric Sensor for Determination of Cesium ion in Environmental samples. *Int. J. Environ. Res.*, **5** (2), 561-566.
- Bhakta, J. N. and Muneke, Y. (2011). Mercury (II) Adsorption onto the Magnesium Oxide Impregnated Volcanic Ash Soil Derived Ceramic from Aqueous Phase. *Int. J. Environ. Res.*, **5** (3), 585-594.
- Camel, V., (2003). Solid phase extraction of trace elements. *Spectrochimica Acta Part B*, **58**, 1177-1233.
- Chen, Q.Y., Wu, Z. H. and Liu, J. L. (2011). Ecotoxicity of Chloramphenicol and Hg Acting on the Root Elongation of Crops in North China. *Int. J. Environ. Res.*, **5** (4), 909-916.
- Dekhil, A. B., Hannachi, Y., Ghorbel, A. and Boubaker, T. Removal of Lead and Cadmium Ions From Aqueous Solutions Using Dried Marine Green Macroalga (*Caulerpa racemosa*). *Int. J. Environ. Res.*, **5** (3), 725-732.
- Dhir, B. and Kumar, R. (2010). Adsorption of Heavy Metals by *Salvinia* Biomass and Agricultural Residues. *Int. J. Environ. Res.*, **4** (3), 427-432.
- Freundlich, H. M. F. (1906). Über die adsorption in lösungen. *Z. Phys. Chem-Frankfurt*, **57A**, 385.
- Hall, K. R., Eagleton, L. C., Acrivos, A. and Vermeulen, T. (1966). Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern condition. *Ind. Eng. Chem. Fundam.*, **5** (2), 212-223.
- Ho, Y. S. and McKay, G., (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.*, **34**, 735-742 .
- Ho, Y. S. (2004). Selection of optimum sorption isotherm. *Carbon*, **42**, 2113-2130.
- Ho, Y. S. and Ofomaja, A. E. (2006). Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochem. Eng. J.*, **30**, 117-123.
- Hubicki, Z., Wawrzekiewicz, M. and Woowicz, A. (2008). Application of Ion Exchange Methods in Recovery of Pd(II) Ions – a Review. *Chem. Anal. (Warsaw)*, **53**, 759-784.
- Jonck, H., (2008). development of platinum metal specific separating agents. *Dissertation*, **1**, 1-7.
- Kargar, M., Khorasani, N. A., Karami, M., Rafiee, G. H. and Naseh, R. (2012). An Investigation on As, Cd, Mo and Cu Contents of Soils Surrounding the Meyduk Tailings Dam. *Int. J. Environ. Res.*, **6** (1), 173-184.
- Langmuir, I. (1916) The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, **38**, 2221.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, **40**, 1361-1403.
- Lemos, V.A., Silva, D.G., Carvalho, A.L., Santana, D.A., dos Santos, G.N. and dos Passos, A.S. (2006). Synthesis of amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry. *Microchemical Journal*, **84**, 14-21.
- Li, P. P., Peng C. S., Li, F. M., Song S. X. and Juan A. O. (2011). Copper and Nickel Recovery from Electroplating Sludge by the Process of Acid-leaching and Electro-depositing. *Int. J. Environ. Res.*, **5** (3), 797-804.
- Mane, P. C. and Bhosle, A. B. (2012). Bioremoval of Some Metals by Living Algae *Spirogyra* sp. and *Spirullina* sp. from aqueous solution. *Int. J. Environ. Res.*, **6** (2), 571-576.
- Naim, R., Kisay, L., Park, J., Lee, C., Qaisar, M., Zulfikar, A. B. and Noshin, M. (2011). Precipitation Chelation of Cyanide Complexes in Electroplating Industry Wastewater. *Int. J. Environ. Res.*, **5** (1), 85-92.

Prabhakaran, D. and Subramanian, M. S. (2003). A column system for the selective extraction of U(VI) and Th(IV) using a new chelating sorbent. *Talanta*, **61**, 423-430.

Redlich, O. and Peterson, D. L. (1959). A useful adsorption isotherm. *J. Phys. Chem.*, **63**, 1024.

Saito, K., Taninaka, I., Yamamoto, Y., Murakami, S. and Muromatsu, A. (2000). Liquid-liquid extraction of platinum (II) with cyclic tetrathioethers. *Talanta*, **51**, 913-919.

Salim, M. and Muneke, Y. (2009). Removal of Arsenic From Aqueous Solution Using Silica Ceramic: Adsorption Kinetics and Equilibrium Studies. *Int. J. Environ. Res.*, **3 (1)**, 13– 22.

Vlasánková, R. and Sommer, L. (1999). Solid Phase Extraction and Preconcentration for the Determination of Trace Amounts of Platinum Group Metals in Environmental and Biotic Material A Critical Review. *Chem. Papers*, **53 (3)**, 200-209

Yu, Ch., Xu, Sh., Gang, M., Chen, G., Zhou, L. (2011). Molybdenum pollution and speciation in Nver River sediments impacted with Mo mining activities in western Liaoning, northeast China. *Int. J. Environ. Res.*, **5 (1)**, 205-212.

Yuh-Shan, H. (2006) .Isotherms for the Sorption of Lead onto Peat: Comparison of Linear and Non-Linear Methods. *Polish Journal of Environmental Studies*, **15 (1)**, 81-86.