



## Ionic imprinted polymers IIPs to determination Vanadium (IV) ion in Crude and Fuel oil

Hassan Noori Mohsen, Yehya Kamal Al-Bayati

Department of Chemistry, College of Sciences, University of Baghdad, Baghdad, Iraq.



CrossMark

### Abstract

A novel Vanadium(IV) ion-imprinted polymers (IIPs) was synthesized by bulk polymerization using different types of monomers such as 1-vinyl imidazole and Styrene, respectively. molar ratios of template, monomer and cross-linking agent for polymerization, solvents and Various monomers were studied to obtain the largest adsorption capacity for Vanadium. The prepared Vanadium-IIPs were characterized using Fourier - transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX) and Scanning electron microscopy (SEM). The process of elution has no influence on the three-dimension network structure surfaces of Vanadium-IIPs. Vanadium(IV) ions could be eluted from IIPs successfully by mixture solution from ethanol and acetic acid. The maximum adsorption capacity of vanadium-IIPs was (568)  $\mu\text{mol/g}$  for Vanadium-IIP1 (using styrene as a monomer) and (491)  $\mu\text{mol/g}$  for Vanadium-IIP2 (using 1-vinyl imidazole as a monomer). The adsorption by Vanadium-IIPs followed a Langmuir isotherm models. Solid-phase extraction (SPE) syringe packed with ionic imprinted polymers (IIPs) were used to selective separation for Vanadium (IV) ion from Crude or fuel oil and digest the polymer to determination the Vanadium by flame atomic absorption spectroscopy (FAAS) Abbreviation IIP-SPE-FAAS.

**Keyword :** Vanadium-Ionic imprinted polymer, adsorption, SPE-FAAS, crude oil, fuel oil

### 1. Introduction

Trace element detection is critical in the petroleum industry since it informs geologists about crude oil sources, movement, and kinds [1]. Vanadium determination is more essential among the first row transition metal ions because vanadium is a pollutants as well as catalytic poisoning in the petroleum cracking processes [2]. Vanadium is present in biological systems and affects the environment through fuel oil combustion, natural sources, and different industrial processes such as ceramics, dyeing, inks, steel manufacture and catalysts. Vanadium is a necessary component of most living organisms [3]. During cracking operations, vanadium is deposited on the surface of the catalyst, reducing its activity and selectivity (raising coke, lowering gasoline and butanes-butylenes) [4]. There are a variety of approaches, like as inductively coupled plasma optical - emission spectrometry (ICP-OES) [5], inductively coupled plasma - mass spectrometry (ICP-MS) [6], and electrothermal atomic absorption spectrometry (ETAAS) [7-9] have been established for the determination of vanadium. ETAAS drew the most attention among these approaches because of its

ease of use, simplicity, and low cost [10]. However, ETAAS, like all of the other approaches, suffers from a lack of sensitivity as well as matrix interference [11]. As a result, an efficient and selective technique for overcoming these challenges and preconcentrating the analyte prior to the determination phase is required. Ion imprinted polymers (IIP) have recently drawn the interest of numerous researchers due to their strong selectivity for imprinted ions and their ability to be used in natural complex matrixes [12]. Continuous advances in analytical chemistry have recently resulted in the creation of novel chemical separation methods that are critical. The development of novel extractants and adsorbents has been fueled by the demand for a more selective system for metal ion separation [13-15].

Currently, the researchers are interested in developing the selective preconcentration of the sorbents used in solid-phase extraction (SPE). This equitable is particularly important when analyzing complex matrixes such as waste water or river water samples.

SPE is simpler, rapid. Economic and environmental-friendly than the traditional liquid-

\*Corresponding author e-mail: [hassan.muhsen1105@sc.uobaghdad.edu.iq](mailto:hassan.muhsen1105@sc.uobaghdad.edu.iq).

Receive Date: 11 June 2021, Revise Date: 05 August 2021, Accept Date: 10 August 2021

DOI: 10.21608/EJCHEM.2021.80139.3952

©2022 National Information and Documentation Center (NIDOC)

liquid extraction. The essential problem associated with SPE columns packed with ordinary stationary phases is the low selectivity of the retention mechanism. A desired grade of selectivity may be reached using columns packed with materials based on molecularly imprinted polymers (MIPs) as selective sorbents [13-15].

Molecular imprinting as a type of special technology is realized by the specific identification. A molecularly imprinted polymer is prepared by mixing the template molecules with functional monomers first. Then the crosslinking agents and initiators are added for polymerization. Later, the template molecules are removed with a chemical or physical method. Certainly, a molecularly imprinted polymer with full of space cavities which match well with the destination molecules is completely prepared [16]. For metal ions, the synthesized sorbent is called ion-imprinted polymer (IIP) which is related to MIPs but it recognizes inorganic ions after imprinting [17]. Various methods, such as bulk polymerization [18], suspension polymerization [19] precipitation polymerization [20], sol-gel polymerization [21, 22], and surface imprinted technique [23, 24] have been used for the preparation of ion imprinted polymers.

In this work, vanadium-IIP was synthesized by bulk polymerization using vanadyl sulphate hydrate as a template with styrene and 1-vinyl imidazole as monomer to prepare two types of vanadium-IIPs with ethylene glycol dimethacrylate (EGDMA) as crosslinker and benzyl peroxide as initiator for removal of V(IV) ions from crude and fuel oil. Effects of monomer and EGDMA dosages on adsorption performance were studied. Adsorption behaviours with various functional monomers, cross-linking agents and solvents were also investigated. SEM, FTIR, and EDX were used to characterize the prepared IIPs. In addition, effects of adsorption conditions, such as adsorption time, flow rate of solution pass-through solid phase extraction syringe and initial vanadium concentration, on adsorption capacity were studied.

## 2. Experimental

### 2.1 Reagents and Chemicals

Styrene, 1-vinyl imidazole, ethylene glycol dimethacrylate (EGDMA) and benzyl peroxide and were purchased from Sigma-Aldrich (St. Louis, MO, USA, [www.sigma-aldrich.com](http://www.sigma-aldrich.com)), methanol, chloroform, acetonitrile, acetic acid, and vanadyl Sulphate hydrate  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$  were purchased from Merck (Darmstadt, Germany, [www.merck.com](http://www.merck.com)). nitrogen gas (99.99%) from Arab gulf factory Baghdad.

### 2.2 Instrument

The control was performed using atomic absorption spectrophotometer instrument (England), the use of UV 1800pc spectrophotometer (Shimadzu, Japan), scanning electron microscopy SEM and EDX MIRA3 TESCAN (Czechoslovakia) FTIR FTIR 8000 (Shimadzu, Japan) and ultrasonic (W.GERMANY) was used to stir up the copolymer solution.

### 2.3 Preparation ionic imprinted polymer

For preparation first vanadium molecularly imprinted polymer (Vanadium-MIP1), 1mmol (0.181 g) from vanadyl Sulphate hydrate ( $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ ) dissolved in little amount of methanol then mixed with 20 mmol (2.08 g) styrene as the monomer, after that added 40 mmol (7.92 g) ethylene glycol dimethacrylate (EGDMA) to the solution as the crosslinker, followed that 0.3 mmol (0.07 g) benzoyl peroxide dissolved in 3ml chloroform and add to the mixture as the initiator. All these materials were dissolved in  $5 \pm 1$  ml methanol ( $\text{CH}_3\text{OH}$ ). While the second vanadium-MIP2 were achieved by mixed the same amount of vanadyl Sulphate hydrate as the template with 20 mmol (1.88g) 1-vinyl imidazole as the monomer after that added 40 mmol (7.92 g) ethylene glycol dimethacrylate (EGDMA) to the solution as the crosslinker and 0.36 mmol (0.08 g) benzoyl peroxide as the initiator which dissolved in  $5 \pm 1$  ml of methanol ( $\text{CH}_3\text{OH}$ ). For obtaining a homogeneous solution, the mixture was shake for 5 minutes.  $\text{N}_2$  passes for 30 minutes on the mixture to extract oxygen from the solution. then, the solution was placed in a water bath at  $60^\circ\text{C}$  overnight. when the reaction completes the molecularly imprinted polymer became hardened, after the polymerization process, the polymer was drying and crashed to obtain a polymer particle. The template extract from MIP by soxhlate in  $\text{CH}_3\text{OH}/\text{CH}_3\text{COOH}$  (30:3 v/v).

Respectfully, Non-molecularly imprinted polymers are made using the same ingredients and circumstances as vanadium-MIP1 and vanadium-MIP2, but without the vanadyl Sulphate hydrate (template.). The same distribution was used in the preparation of non-imprinted polymers (NIPs), but without the template.

### 2.4 sampling procedure

Prepare a stock solution 1000 ppm of Vanadium in organic medium by dissolved (0.887 gm) from

Vanadyl sulphate hydrate in little amount of methanol and add base oil to complete volume 250ml and use to prepare a series of concentration (1, 50, 100, 200, 300, 400, 500, 600, 700, 800 ppm). 1 ppm solution diluted to prepare (0.1, 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 25 ng) for preconcentration method to determination the little amount note detect direct in flame atomic absorption spectrophotometer. Also, brought several samples of crude and fuel oil.

### 2.5 The Sampling Device

A 3 ml solid phase extraction syringe was used and each syringe was filled with different weights (0.1 and 0.2gm) from IIPs.

### 2.6 Extraction and digestion procedure

Vanadium(IV) ion was extracted from synthetic solution, diluted synthetic solution and crude or fuel oil using Vanadium-IIP1 (styrene as a monomer) and Vanadium-IIP2 (1-vniyl imidazole as a monomer) by solid phase extraction (SPE) syringe. This syringe was prepared by packing it with a IIP, 0.2mg, the size of its container 5ml. The solution containing Vanadium pass through SPE syringe by vacuum process using peristaltic pump in different rate.

IIP was collected from column in the small beaker, dried for 60 minutes, than a 1mL of concentrated sulfuric acid is added to it and left for a 8 minute, the next step concentrated nitric acid 1ml is added to it and heated at a 60 temperature after that added deionized water to the mixture, later estimated directly by flame atomic absorption spectrophotometer.

## 3. Result and dissection

### 3.1. Characterizations

#### 3.1.1. FT-IR

Spectral analysis was used to determine the interaction between Vanadium (IV) ion and monomer. The Cesium Iodide (CsI) pellet technique registered the FT-IR spectrum in the range of 250–4000  $\text{cm}^{-1}$ . The FT-IR spectra of Vanadium-IIP1 before and after elution are shown in **Fig.(1)**. It can be seen that both spectra have similar backbones, mean that the elution process has nearly no influence on the primary polymer network structure. The spectrum of vanadium-IIP1 before elution has strong bands at 474.10, 1654.10, corresponding to VO-S and VO-O groups, which indicates that Vanadyl sulphate hydrate had participated in the synthesis of vanadium-IIP1. However, these tow peaks disappear after eluting V(IV) ions due to destruction of original interaction between styrene and  $\text{V}^{2+}$ , indicating that  $\text{V}^{4+}$  had been removed successfully.

The FT-IR spectra of Vanadium-IIP2 are shown in **Fig.(2)** where a appears band at 472.53 , 1655.95  $\text{cm}^{-1}$  corresponding to VO-S and VO-O groups.

These two peaks disappear after eluting V(IV) ions due to the destruction of original interaction between 1-vniyl imidazole and  $\text{V}^{4+}$ . The main peaks obtained from figures list in the table (1) and table (2).

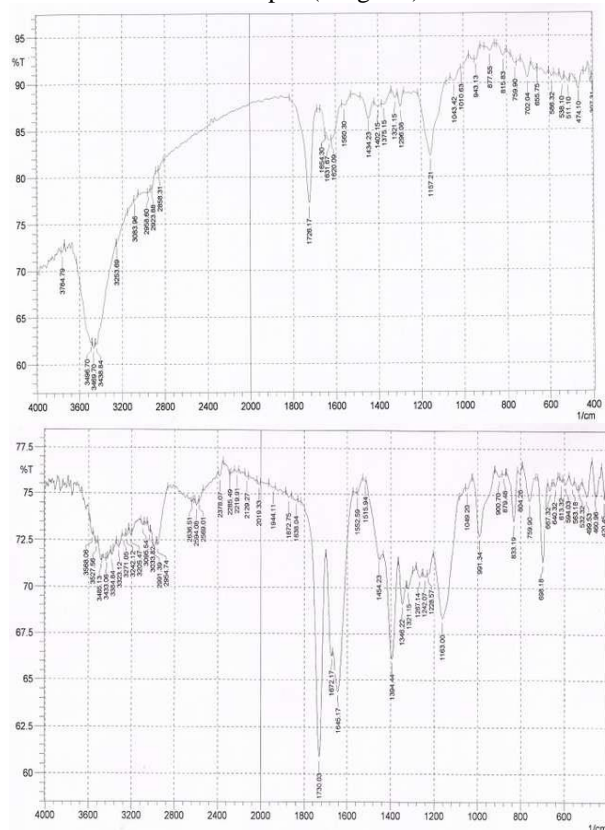
### 3.1.2. SEM

Morphological analysis is an important characteristic for understanding the size and arrangement of areas where Vanadium ion was removed.

The morphology of the V-IIPs was evaluated by SEM images.

For Vanadium-IIP1 **Fig.3(A,B)** shows the surface morphologies of the particles before and after elution. It can be seen that the surface of eluted Vanadium-IIP1 is containing pores and rougher than that of non-eluted one as a result of the removing of V(IV) ions.

surface morphologies of Vanadium-IIP2 before and after elution shown in **Fig.4(A,B)**. for tow kind of prepare IIPs shows numerous pores on the surface which made it a suitable sorbent because of the well-defined binding sites on the imprinted polymer. In addition, the images shows that the diameters of pores ranging between (200-300 nm) for vanadium-IIP1 and (100-150 nm) for Vanadium-IIP2 are uniform in sizes and shapes (irregular)



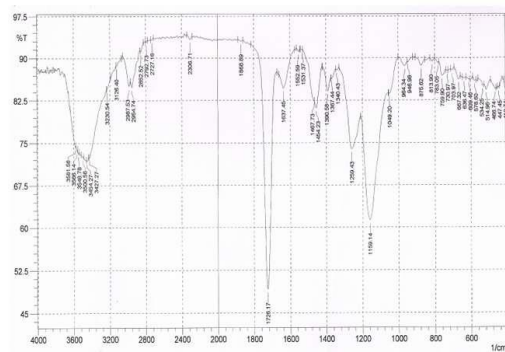
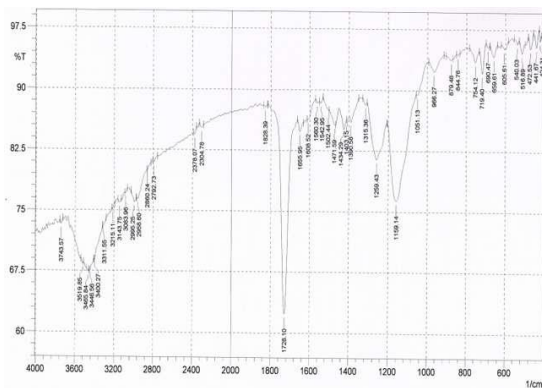
**FIG. 1.** FTIR spectrum of Vanadium-IIP1(Using styrene as a monomer). A.before the removal of V(IV)B. after the removal of V(IV)

**Table (1):** The most identified peaks of FTIR spectrum Vanadium-IIP1 using (styrene) as a functional monomer

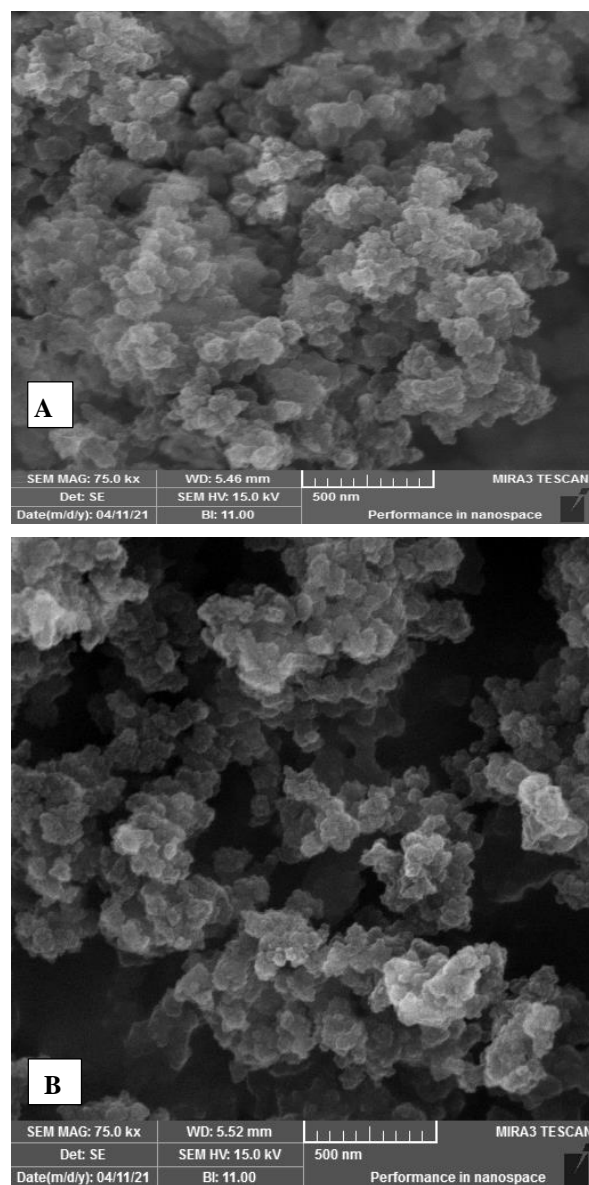
NO	Functional Group	Ni(NO <sub>3</sub> ) <sub>2</sub> . 6H <sub>2</sub> O	Nickel-IIP1 before templet removal	Nickel-IIP1 after templet removal
1	C-H aliphatic	-----	2995.25 2962.46	2991.39 2958.60
2	C=O ester	-----	1724.24	1731.96
3	C-H aromatic	-----	3095.54	3020.32
4	C=C aliphatic	-----	1554.52	1552.59
5	CH <sub>2</sub> =CH <sub>2</sub> aromatic	-----	1604.66	1610.45
6	C-O	-----	1298	1298.08
7	Ni-N	823.55	823.83	-----
8	N-O	1376.0	1371.29	-----
9	N=O	1620	1637.45	-----

**Table (2):** The most identified peaks of FTIR spectrum Vanadium-IIP2 using (1-vinyl imidazole) as monomer

NO	Functional Group	VOSO <sub>4</sub> .H <sub>2</sub> O (cm <sup>-1</sup> )	Vanadium-IIP1 before templet removal (cm <sup>-1</sup> )	Vanadium-IIP1 after templet removal (cm <sup>-1</sup> )
1	C-H aliphatic	-----	2958.60 2990.31	2954.74 2991.39
2	C=O ester	-----	1726.17	1730.03
3	C-H aromatic	-----	3083.96	3095.54
4	C=C aliphatic	-----	1560.30	1552.59
5	CH <sub>2</sub> =CH <sub>2</sub> aromatic	-----	1631.67	1645.17
6	C-O	-----	1296.08	1267.14
7	VO-S	474.81	474.46	-----
8	VO-O	1654.81	1654.30	-----

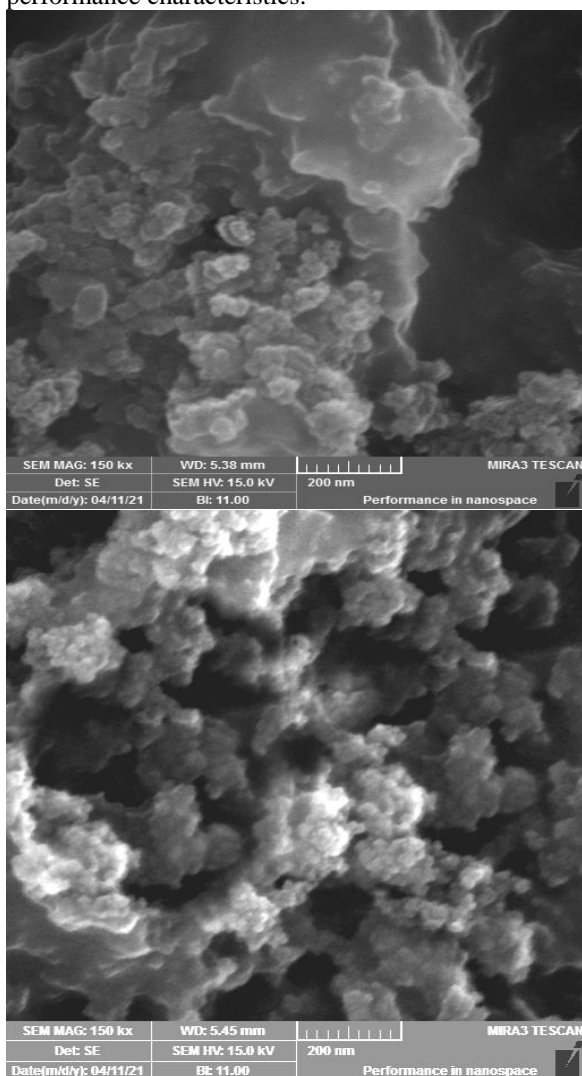
**FIG.2.** FTIR spectrum of Vanadium-IIP2

(Using 1-vinyl imidazole as a monomer).

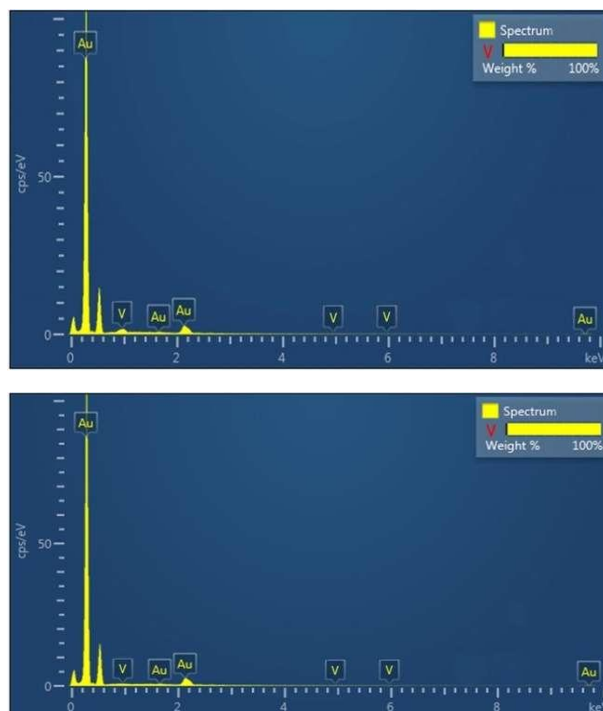
**A.** before the removal of V(IV) **B.** after the removal of V(IV)**FIG. 3.** SEM of Vanadium-IIP1 (Using styrene as a monomer).**A.** before the removal of V(IV) **B.** after the removal of V(IV)

### 3.1.3. EDX

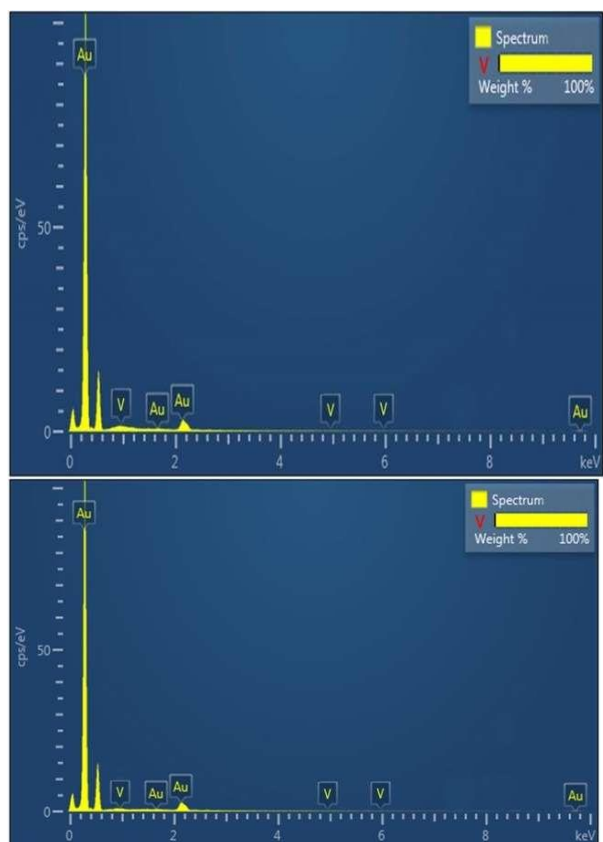
The EDX teste was used to determine the composition of Vanadium-IIPs and approve that the V(IV) ion was eluted successfully. The EDX spectra of Vanadium -IIPs before and after elution are shown in **Fig.(5,6)**. The results in Fig. 5A and 6A confirm the presence V (IV)in the structure. As shown in **Fig 5B and 6B**, V (IV)ion is not present in the structure of vanadium-IIPs after elution, indicating that the elution of V(IV) ion with porogen solvent CH<sub>3</sub>OH/CH<sub>3</sub>COOH (30:3 v/v) successfully. Several experiments were conducted to determine o the optimal ratios of vanadium ion: monomer: cross linker for preparing molecularly imprinted polymers and non-imprinted polymers. Table (3) shows the ideal ratios for creating MIPs and NIPs with the best performance characteristics.



**FIG.4.** SEM of Vanadium-IIP2 (Using 1-vinyl imidazole as a monomer). **A.** before the removal of V(IV) **B.** after the removal of V(IV)



**FIG. 5.** EDX spectrum of Vanadium-IIP1(Using styrene as a monomer). **A.**before the removal of V(IV) ion **B.** after the removal of V(IV) ion

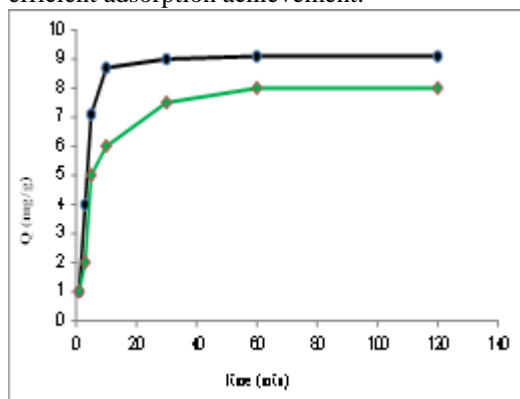


**FIG.6.** EDX spectrum of Vanadium-IIP2(Using 1-vinyl imidazole as a monomer). **A.** before the removal of V(IV) ion **B.** after the removal of V(IV) ion

### 3.3. Adsorption condition

#### 3.3.1. Adsorption time

Adsorption rate is an important parameter in the industrial application of prepared IIPs. Variations in adsorption capacity with respect to adsorption time (1, 3, 5, 10, 30, 60, and 120 min) were studied and the results for two IIPs are shown in **Fig.(7)**. The adsorption capacity increases sharply in the first 5 minutes, indicating that the adsorption process of V (IV) ion in aqueous solution with prepared V-IIPs is very fast at the beginning. Then the adsorption capacity increases lightly with increasing adsorption time from 5 min to 10 min and remains unchanged after 10 min. Very fast adsorption kinetics establish that the binding sites in prepared Vanadium-IIPs have excellent affinity to V (IV) ions, leading to high efficient adsorption achievement.



**FIG.7.** Time-dependent changes in adsorption capacity (20 mL 50 mg.L<sup>-1</sup> Vanadium solution, 100 mg IIPs, 25°C).

**Table (3)** The variation ratios of templet, monomer, crooslinker and solvent in the preparation of Vanadium - IIPs and NIPs

NO. of IIP	Ratio	salt VOSO <sub>4</sub> .H <sub>2</sub> O	Monomer Styrene	Cross linker EGDMA	Initiator	Solvent	Result
IIP1	%	26.24	26.23	47.04	0.3	6ml CH3OH	Salt Precipitate at the bottom
	mmole	2.762	2.76	4.95	0.3		
IIP1	%	2.68	47.73	48.65	0.3	6ml CH3OH	Pile white gel
	mmole	0.552	9.81	10.00	0.3		
IIP1	%	1.73	32.72	65.25	0.3	6ml CH3OH	White rigid
	mmole	1	20.0	40.0	0.3		
NIP1	%	-----	7.010	92.63	0.3	6ml CH3OH	White rigid
	mmole	-----	0.3	3.964	0.3		
		salt VOSO <sub>4</sub> .H <sub>2</sub> O	Monomer 1-vinyl imidazole	Cross linker EGDMA	Initiator	Solvent	Result
IIP2	%	18.15	40.36	41.18	0.3	6ml CH3OH	Salt Precipitate at the bottom
	mmole	2.209	4.91	5.01	0.3		
IIP2	%	3.08	34.04	62.57	0.3	6ml CH3OH	Salt Precipitate at the bottom
	mmole	0.500	5.511	10.13	0.3		
IIP2	%	1.63	32.62	65.25	0.3	6ml CH3OH	White rigid
	mmole	1	20.0	40.0	0.3		
NIP2	%	-----	7.010	92.63	0.3	6ml CH3OH	White rigid
	mmole	-----	0.3	3.964	0.3		

A. Vanadium-IIP1(Using styrene as monomer)

B. Vanadium-IIP2(Using 1-vinyl imidazole as monomer)

#### 3.3.2. Maximum adsorption capacity

Appraise the adsorption achievement of vanadium-IIPs, the effect of initial Vanadium ion concentration ranging from (0.196) to (13.72) μmol/ml on adsorption capacity was studied using the following equation.

$$Q = \frac{(C_i - C_f)V_s \times 1000}{M_{MIP}} \quad \text{----- (1)}$$

where Q is the binding capacity of MIPs (μmol/g), C<sub>f</sub> is the final Vanadium concentration (μmol/ml), C<sub>i</sub> is the initial Vanadium concentration (μmol/ml), V<sub>s</sub> is the volume of solution tested (ml) and M<sub>MIP</sub> is the mass of dried polymer (mg).

As shown in **Fig(8)**, the adsorption capacity increases sharply at first and gradually increasing with rise the concentration of Vanadium(IV) ion. Mass transfer driving force acts by the difference between the concentration of Vanadium ion in bulk solution and around surface of IIPs increases with the increase of initial Vanadium ) ion concentration, which significantly increases the equilibrium adsorption capacity. However, when the Vanadium concentration is higher than 8 μmol/ml, the amount of adsorbed metal constant.

Tables (4,5) and shows the adsorption capacity if Vanadium -IIP1 and Vanadium -IIP2 respectively. Langmuir isotherm models may be used to calculate Vanadium -IIPs' maximal adsorption capacity. shown in Fig(9). The maximum adsorption capacity is (568) $\mu\text{mol/g}$  for Vanadium -IIP1 and (491) $\mu\text{mol/g}$  for Vanadium -IIP2. The Vanadium -IIPs prepared in this work has the high adsorption capacity. The uniform and attainable imprinted binding sites greatly enhance the adsorption execution of Vanadium ions by the prepared V-IIPs. Moreover, the binding between monomers and Vanadium is very stable, allowing for simpler chelation formation. The Langmuir adsorption isotherm equation shown in the following

$$\frac{Q}{C_{\text{free}}} = \frac{Q_{\text{max}} - Q}{K_d} \dots\dots\dots (2)$$

where  $Q$  is the binding capacity,  $Q_{\text{max}}$  is the maximum apparent binding capacity,  $C_{\text{free}}$  is the free analytical concentration at equilibrium ( $\mu\text{mol/L}$ ), and  $K_d$  is the dissociation constant at binding site. In a linear plot of  $Q/C_{\text{free}}$  vs.  $Q$ , the equilibrium dissociation constant was estimated from the slopes, and the apparent maximum number of binding sites was derived from the y-intercepts.

### 3.4. Application

#### 3.4.1. Determination of V (IV)ion in synthetic organic solution

Series of synthetic solution was prepared to studied the recovery of SPE-FAAS by using Vanadium-IIPs shows in table (6)

#### 3.4.2 preconcentration in organic solution

Preparation of 100 ml of sample containing 5.0 ng/ml of Vanadium (IV) ion by using deionized water were loaded into the Vanadium-IIPs SPE syringe at 1.0 ml/min. After the sample loading, For 5 minutes, air was circulated through the column. Then, Vanadium-IIP was collected from column in the small beaker and add 1mL of concentrated sulfuric acid left for a 8minute. After that concentrated nitric acid 1ml is added to it and heated at a 60 temperature and added distilled water to the mixture to complete volume to 5ml, later estimated directly by flame atomic absorption spectrophotometer. The loading of 100 ml water sample with an digest volume 5ml

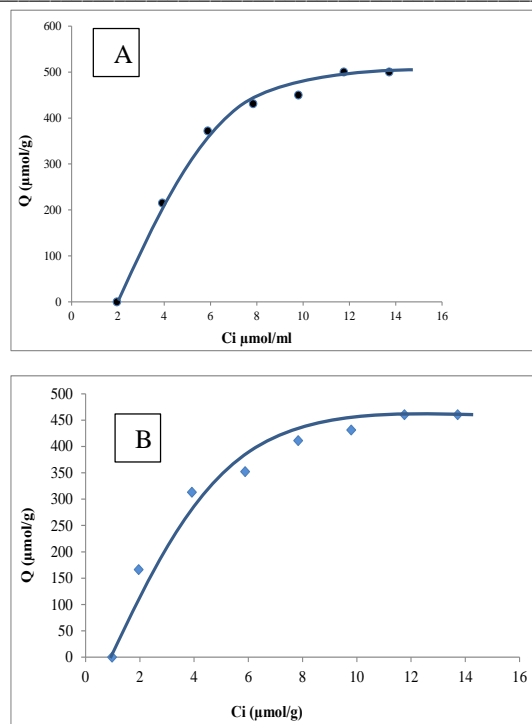


Fig.(8) the relationship between adsorption capacity and initial V(IV) ion : A. for Vanadium-IIP1 B. for Vanadium-IIP2

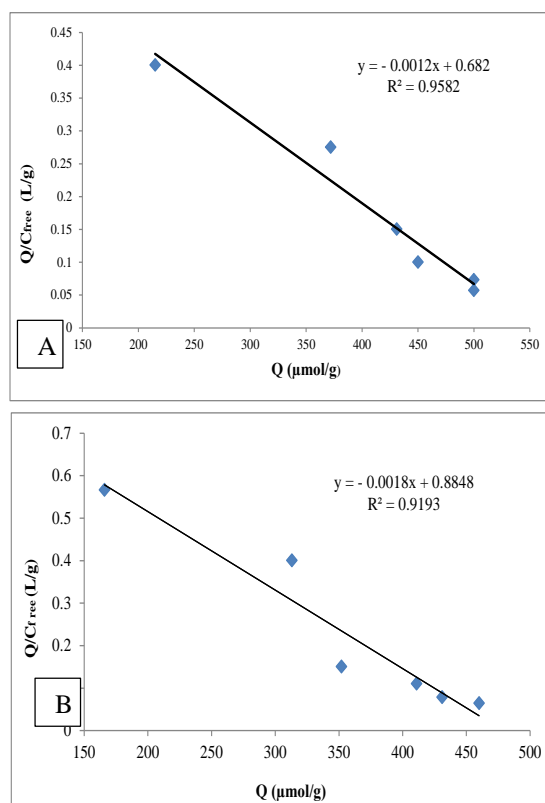


Fig.(9) the relationship between  $Q/C_{\text{free}}$  (L/g) and adsorption capacity to calculate maximum adsorption capacity A. for Vanadium-IIP1 B. for Vanadium-IIP2

**Table (4)** the results of the adsorption capacity experiments for Vanadium-IIP1 and their relationship with the initial concentration

$C_i$ ( $\mu\text{mol/ml}$ )	$C_f$ ( $\mu\text{mol/ml}$ )	$C_i-C_f$ ( $\mu\text{mol/ml}$ )	$Q$ ( $\mu\text{mol/g}$ )	$Q/C_f$ ( $\text{L/g}$ )
0.196	0	0	0	0
0.862	0	0	0	0
1.96	0	0	0	0
3.921	1.764	2.156	215	0.4
5.882	2.156	3.725	372	0.275
7.843	3.529	4.313	431	0.15
9.80	4.313	4.509	450	0.1
11.76	6.764	5.00	500	0.073
13.72	8.725	5.00	500	0.057

**Table (5)** the results of the adsorption capacity experiments for Vanadium-IIP1 and their relationship with the initial

$C_i$ ( $\mu\text{mol/ml}$ )	$C_f$ ( $\mu\text{mol/ml}$ )	$C_i-C_f$ ( $\mu\text{mol/ml}$ )	$Q$ ( $\mu\text{mol/g}$ )	$Q/C_f$ ( $\text{L/g}$ )
0.196	0	0	0	0
0.98	0	0	0	0
1.96	0.294	1.666	166	0.566
3.921	0.784	3.137	313	0.40
5.882	2.352	3.529	352	0.150
7.843	3.725	4.117	411	0.110
9.80	5.49	4.313	431	0.078
11.76	7.156	4.607	460	0.064
13.72	8.941	4.607	460	0.050

**Table (6)** the results of the determination of Vanadium ion in synthetic organic solutions

NO.	Concentration V(IV)ion ( $\mu\text{g/ml}$ )	V(IV)ion found ( $\mu\text{g/ml}$ )	Recovery
1	1	0.99	99
2	5	4.98	99.6
3	10	9.85	98.5
4	20	19.93	99.6
5	30	30.07	100.2

Results in a potential 20-fold concentration increase in the analytes for each extraction technique taken into account. Assuming we have a quantitative recovery, it is a concentration of 5–25 ng/ml, a value that is easily quantifiable by GFAAS but not by FAAS.

The characteristic performance information for the Vanadium-IIP2 SPE and preconcentration procedure as shown in table(7). The precision of the method for a standard, evaluated as the relative standard deviation ( $n = 8$ ) was 5.0 ng/ml of V(IV) ions. The limit of detection, defined as the concentration of analyte that generates signals that are three times the blank's standard deviation plus the net blank's standard deviation ferocity for 100 ml of sample volume, were 5 ng/ml

**Table (7)** Preconcentration procedure performance characteristics

Specification	V
Detection limit	5 ng/ml
precision	3.7
Linear rang	5 - 25 ng/ml
Equation of regression	AA = 6.659 $C_V$ - 0.0001

### 3.4.3. Determination of V(II) ion in Crude and fuel oil .

Crude and fuel oil samples have been brought from refinery . Then, these solutions were introduced into the Vanadium-IIP-SPE packed column system in the same manner as described previously. The obtained results as well as the recovery tests shown in table(8)

**Table (8)** determination of V (IV) ion in Crude and fuel oil

Samples	Vanadium (II) ion add (ppm)	Vanadium (II) ion found (ppm)	Recovery (%)
Crude oil 1	0.0	57.2 $\pm$ 1.5	-
	10.00	66.4 $\pm$ 1.4	98.8
	15.00	71.8 $\pm$ 0.9	99.4
	20.0	77 $\pm$ 2.1	99.7
Crude oil 2	0.0	70.06 $\pm$ 0.21	-
	10.00	79.00 $\pm$ 1.5	98
	15.00	84.5 $\pm$ 2.1	99.4
	20.0	90.50 $\pm$ 1.5	100.4
Fuel oil 3	0.0	103 $\pm$ 2.3	-
	10.00	111.5 $\pm$ 1.9	98.6
	15.00	117 $\pm$ 1.5	99.1
	20.0	122.4 $\pm$ 1.2	99.5

## 4. Conclusion

Novel Vanadium-IIPs was prepared by bulk polymerization. Styrene and 1-vinyl imidazole selected as functional monomer and EGDMA as crosslinker. Besides, benzyl peroxide was used as an initiator in the presence of chloroform solvent. The optimal molar ratios of Vanadium (IV) ion to monomer and crosslinker dosage were studied. The irregular shapes and three-dimension network structure of polymers it was possible to notice by SEM. The results of FT-IR and EDX proved the successful elution of V(IV)ions by



**CH<sub>3</sub>OH/CH<sub>3</sub>COOH (30:3 v/v)** solution. Effects of operating time and initial Vanadium (IV) ion concentration on adsorption performance were investigated. Adsorption by IIPs was fast (adsorption equilibrium was reached within 10 min) and followed Langmuir isotherm models. The maximum adsorption capacity of the IIPs is (568)  $\mu\text{mol/g}$  for Vanadium-IIP1 and (491)  $\mu\text{mol/g}$  for Vanadium -IIP2, which is higher than other sorbents reported in literatures. The elution process has nearly no influence on cavity structure and chemical property of the polymers, indicating that Vanadium -IIPs have excellent stability and regeneration capabilities.

### Acknowledgements

This work was supported by Petroleum research and development center / ministry of oil and Service laboratories of College of Sciences, University of Baghdad .

### References

1. Al-Swaidan HM, The determination of lead, nickel and vanadium in Saudi Arabian crude oil by sequential injection analysis/inductively-coupled plasma mass spectrometry. *Talanta* 43,(1996) ,1313.
2. Murillo M, Chirinos J, Use of emulsion systems for the determination of sulfur, nickel and vanadium in heavy crude oil samples by inductively coupled plasma atomic emission spectrometry. *J Anal At Spectrom*, 9,(1994),237.
3. Filik, H., Yanaz, Z., Apak, R., Selective, determination of total vanadium in water samples by cloud point extraction of its ternary complex. *Anal. Chim. Acta*, 620,(2008),27–33.
4. Valkovic V , Trace elements in petroleum. The Publishing Co.,Tulsa(1978)
5. Brown RJ, Determination of trace metals in petroleum and petroleum products using an inductively coupled plasma optical emission spectrometer. *Spectrochim Acta B*, 38, (1983), 283.
6. BettinelliM, Spezia S, Baroni U, Bizzarri G Determination of trace elements in fuel oils by inductively coupled plasma mass spectrometry after acid mineralization of the sample in a microwave oven. *J Anal At Spectrom*, 10, (1995), 555.
7. Pekiner OZ, emullah N, Tüzen M , Preconcentration and speciation of vanadium by three phases liquid-liquid microextraction prior to electrothermal atomic absorption spectrometry. *J Ind Eng Chem*, 10, (2013), 1016.
8. Wadhwa SK, Tuzen M, Kazi TG, Soylak M, Graphite furnace atomic absorption spectrometric detection of vanadium in water and food samples after solid phase extraction on multiwalled carbon nanotubes. *Talanta*, 11, (2013), 205.
9. Emullah N, TuzenM, Kazi TG, Citak D, Soylak M, Pressureassisted ionic liquid dispersive microextraction of vanadium coupled with electrothermal atomic absorption spectrometry. *J Anal At Spectrom*, 28, (2013), 1441.
10. Veschetti E, Maresca D, Lucentini L, Ferretti E, Citti G, Ottaviani M, Monitoring of V(IV) and V(V) in Etnean drinking-water distribution systems by solid phase extraction and electrothermal atomic absorption spectrometry. *Microchem J*, 85, (2007), 80.
11. Nukatsuka I, Shimizu Y, Onzeki K, Determination of V(IV) and V(V) by electrothermal atomic absorption spectrometry following selective solid-phase extraction and the study on the change in the oxidation state of vanadium species in seawater during the sample storage. *Anal Sci*, 18, (2002), 1009.
12. Andac M, Senel S, Say R, Denizli A, Ion-selective imprinted beads for aluminum removal from aqueous solutions. *Ind Eng Chem Res*, 45, (2006), 1780.
13. J. Scancar, R. Milacic, A novel approach for speciation of airborne chromium by convective-interaction media fast-monolithic chromatography with electro thermal atomic-absorption spectrometric detection, *Analyst* 127 (2002) 629.
14. V.M. Biju, J.M. Gladis, T.P. Rao, Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications *Anal. Chim. Acta* 478 (2003) 43.
15. R. Say, E. Birlik, A. Ersöz, F. Yılmaz, T. Gedikbey, A. Denizli, Preconcentration of copper on ion-selective imprinted polymer microbeads *Anal. Chim. Acta* 480 (2003) 251.
16. L.I. Andersson, Efficient sample pre-concentration of bupivacaine from human plasma by solid-phase extraction on molecularly imprinted polymers *Analyst* 125 (2000) 1515.
17. C. Crescenzi, S. Bayouhd, P.A.G. Cormack, T. Kklein, K. Ensing, Efficient sample pre-concentration of bupivacaine from human plasma by solid-phase extraction on molecularly imprinted polymers, *Anal. Chem.*73 (2001) 2171.
18. O. Vigneau, C. Pinel, M. Lemaire, Ionic imprinted resins based on EDTA and DTPA derivatives for lanthanides (III) separation, *Anal. Chim. Acta* 435 (2001) 75.
19. Xue Zhanga, Jian Yanga, Chao Wang, Yakun Suna, Zhaosheng Liua, Yanping Huang,., Haji Akber Aisaa, Improving imprinting effect by reducing sites embedding: Selective extraction of 1,2,3,4,6-penta-O-galloyl- $\beta$ -D-glucose from *Paeonia lactiflora* Pall by hydrophilic molecularly imprinted polymers based on macromonomer and metal ion pivot, *Microchemical Journal*, 158 (2020) 105140.

20. Mohammad Behbahani, Mohsen Taghizadeh, Akbar Bagheri, Hadi Hosseini, Mani Salarian, Atieh Tootoonchi, A nanostructured ion-imprinted polymer for the selective extraction and preconcentration of ultra-trace quantities of nickel ions, *Microchim Acta* 178 (2012) 429-437.
21. M.Behbahani, A.Bagheri, M.Taghizadeh, M. Salarian, O.Sadeghi, L.Adlnasab, K.Jalali, Synthesis and characterisation of nano structure lead (II)ion-imprinted polymer as a new sorbent for selective extraction and preconcentration of ultra trace amounts of lead ions from vegetables, rice, and fish samples, *Food Chem.* 138 (2013) 2050–2056.
22. M. Gawin, J. Konefał, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec, E. Witek, Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium(II) via flow-injection-flame atomic absorption spectrometry, *Talanta* 80 (2010) 1305–1310.
23. J. Otero-Romani, A. Moreda-Pineiro, P. Bermejo-Barrera, A. Martin-Esteban, Inductively coupled plasma-optical emission spectrometry/mass spectrometry for the determination of Cu, Ni, Pb and Zn in seawater after ionic imprinted polymer based solid phase extraction, *Talanta* 79 (2009) 723–729.
24. C.A. Quirarte-Escalante, V. Soto, W.D.L. Cruz, G.R. Porras, R. Manriquez, S.Gomez-salazar, Synthesis of hybrid adsorbents combining sol-gel processing and molecular imprinting applied to lead removal from aqueous streams, *Chem. Mater.* 21 (2009) 1439–1450.
25. G.Z. Fang, J. Tan, X.P. Yan, An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium(II), *Anal. Chem.* 77 (2005)1734–1739.
26. Y.C. Zhan, X.B. Luo, S.S. Nie, Y.N. Huang, X.M. Tu, S.L. Luo, Selective separation of Cu(II) from aqueous solution with a novel Cu(II) surface magnetic ion-imprinted polymer, *Ind. Eng. Chem. Res.* 50 (2011) 6355–6361.
27. Z.C. Li, H.T. Fan, Y. Zhang, M.X. Chen, Z.Y. Yu, X.Q. Cao, T. Sun, Cd(II)-imprinted polymer sorbents prepared by combination of surface imprinting technique with hydrothermal assisted sol-gel process for selective removal of cadmium from aqueous solution, *Chem. Eng. J.* 171 (2011) 703–710.