An Analytical Study of Complexation Effect of Cd(II) Ion with Polystyrene Boned Functional Group in the Presence of Third Component γ-Dinitrophenol and α- Dinitrophenol in Aqueous Solutions

Badr Ismail Abdul-Razzak[1], Ali Saad Alwesabi[2]

[1]Department of Chemistry, Faculty of Education, Hodeidah University, Yemen.
[2]Department, Faculty of Pharmacy, University of Science and Technology, Yemen.

Corresponding Author's E-mail: badrasml@gmail.com

Abstract

This study tackles a selective, sensitive and reliable method for preconcentration and spectrophotometric determination of trace cadmium ions in its aqueous solutions based on information of mixed-ligand complex in the (complexingabsorbent-Cd(II)ions- α- and γ-dinitrophenol) system. The effect of adding α- and γ-dinitrophenol ligands on complexation of Cd (II) with adsorbents of polystyrene-azo-phenol derivatives in aqueous solutions was investigated. The parameters including optimum acidity (pH_{opt}), the half-adsorption pH value (pH_{50}), time (t) and temperature (T), the adsorption capacity (q_m), the stability constant of the complexation (logβ) in the presence of a ligand as a third component were extensively investigated under batch (static) conditions. The adsorption selectivity of Cd (II) and the possibility of desorption in this system were studied. The structure of the mixed ligand complex was suggested.

Keywords: Cadmiumions Chelating group, Desorption and Adsorption, Efficiency and Selectivity, Polystyrene-azo-phenol, α- and γ-dinitrophenol, Quantitative adsorption.

Introduction

The determination of the trace-quantities of heavy metals in aqueous solutions is one of the most important analytical problems due to the possible delivery of the toxicant into environmental samples in the concentrations above the safe limits. Cadmium exposure is a risk factor associated with a large number of illnesses including kidney disease (1) early atherosclerosis, hypertension, and cardiovascular diseases (2).

The modern instrumental analysis methods do not always allow the direct determination of trace elements due to influence of the matrix composition of the sample or the low concentrations of the elements being determined in order to overcome this problem, studies have been performed for removal efficiencies of trace quantities of harmful heavy metals from wastewater using low-cost adsorbents with high adsorption capacity. In recent years, adsorption methods have been widely used with the chelating polymer adsorbents for separation and preconcentration of harmful trace elements from their solutions at levels from 10^{-5}-10^{-8} % (3, 4, 5).

The ternary complex adsorbents in which metal ion attached to two different ligands like ($ligand_1$-M^{+n}– $ligand_2$) are important in analytical processes and metallic-catalyzed reactions. The use of this system has received wide acceptance because these complex polymer adsorbents present enhanced strength and high color intensity with colored complexes; these complexes formed at lower acidic values, they are better extractable, act (6).

In these systems, the coordination capacity of a multi-charged cation is highest or complete to exclude the occurrence of masking, hydrolysis and solvolysis reactions, which result in a partial weakening of bonds in the complex and in a decrease in its stability (7, 8). Heretofore, we previously studied the complexation of Cd(II) with a group of synthesized sorbents based on aminopolystyrene and substituted phenols having structurally different substituent's of various electronic natures in the para position with respect to phenolic hydroxyl like Br, NO_2, SO_3H, COOH, CH_3 and NO_2.

Since the coordination number of the Cd (II) cation is 4, this property is incompletely realized in a complex with the given structure (Figure 1). Therefore, we studied the interaction of a third component with a group capable of forming a valence bond with Cd (II) ion .This choice of a third component allowed us to monitor the effect of the nature of this component on the pH of complexation and the adsorption of Cd (II) at the active chelating groups of the adsorbent.Therefore, the aim of this work to study the formation reactions of the ternary systems of (adsorbent- Cd (II) ions -α- and γ-dinitrophenol) and the most important parameters of Cd(II) chemisorption with third components with different electronic structures.

Materials

Polystyrene-azo-phenol derivatives were applied to adsorb the trace amount of elements in the model aqueous solutions. The structure and the nomenclatures of these adsorbents are shown in Table (I) and Figure (1) This class of adsorbents was purchased from Central Chemical Laboratory of IGEM, Russian Academy of Sciences.

The adsorbents were synthesized according to procedures in (9). They were ground in an agate mortar and bolted through a sieve of 200 mesh (0.074 nm) (10).

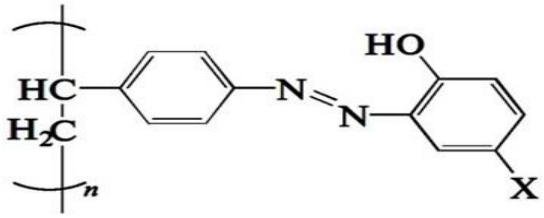

Figure 1: The structure of the adsorbents (PSAHB-X)
where X: H, Br NO_2,COOH,NH_2 or SO_3H

Table 1: Nomenclature of our complex polymer adsorbents under study

No.	Name of Adsorbent	Abbreviation
1	Polystyrene(4-azo-1')-2'-hydroxy-5'-benzene	PSAHB-H
2	Polystyrene(4- azo-1')-2'-hydroxy -5'-chlorobenzene	PSAHB-Br
3	Polystyrene(4-azo-1')-2'-hydroxy-5'-nitrobenzene	PSAHB-NO_2
4	Polystyrene(4-azo-1')-2'-hydroxy-5'-sulfobenzene	PSAHB- SO_3H

Cadmium (II) stock solutions were 1 $mg.L^{-1}$(1000 ppm, 0.017 M Cd (II)) and the working standard solutions were prepared in the range of 1 to 100 ppm by successive dilution of the stock solution. To create the required pH values, 0.1M standard solutions of HCl (for pH: 0.5-2) and ammonia-acetate buffer solutions (for pH: 2.5-11) were used. A solution of γ-Dinitrophenol andα-Dinitrophenol were Sigma-Aldrich (99.99%)with a concentration of 25µg/mL, (it was experimentally determined). A 200 / 0.0001g 0.1mg digital analytical balance TOPLAB India,a781 pH/Ion meter with accuracy ±0.05pH,China 78-1 magnetic stirrer with hot plate, UV-VIS Spectrophotometer S-927 Systonic India were used in the present study.

Excremental methods

Calibration curve of standard cadmium solutions was constructed with15 standards in the range 1 - 15µg/ml. The required amount of a third component for quantitative adsorption was studied by preparing a series of solutions with the constant concentration of Cd(II) ions (i.e. 25µg) and 25 mg of adsorbent in 25 mL of aqueous solution, and variable multiple amounts of a third component ranging from 0 to100µg/ml with respect to the element. Optimal pH values of Cd (II) adsorption pH_{opt} were determined experimentally from the plots of adsorption degree (R%) versus the solution's pH ranged from 1 to 10. For this purpose, 20 stoppered bottles with 40 mL volume each one contained 25 mg of adsorbent under study, 25 µg of Cd(II)(C_0) and 30 µg/ml γ-Dinitrophenol (as third component) were added .Then the required volume of aqueous buffer solution was added to adjust the pH in the range from 1 to 10, the total volume was brought to 25 mL and the mixture stirred by a magnetic stirrer for 2 hours at 25°C. Then, the adsorbent was collected on a blue ribbon filter paper with pore

size 0.45 μm. The absorbance (A) of Cd(II) in the filtrate determined by a UV-Vis spectrophotometry with xylenol orange reagent (pH 6.2, λ_{max} = 580 nm, I = 1 cm)] , then the amount of cadmium in the filtrate C_s was calculated from a straight-line equation of calibration curve of standard cadmium solutions. The amount of adsorbed Cd(II)ions (q_m) calculated using Eq.(1)**:**

$$q_m = C_0 - C_e \qquad (1)$$

The adsorbent degree of cadmium (R %) at the created pH values was calculated from

$$R,\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

These data used to create the graphs of R(%)versus solution's pH . From these graphs, the pH_{opt} corresponded to the highest R% and the values of pH_{50} at R = 50% were determined graphically. According to the observed data, we determine the best adsorbent with α- and γ-dinitrophenol.

Effect of contact time and solution temperature

The effect of contact time and solution temperature on cadmium adsorption (R %) were investigated. For this purpose, three sets of solutions each contains 25 μg of Cd (II), 25 mg of a adsorbent and 30μg of a third component were prepared. The pH was adjusted with the optimal acidity determined previously. The solutions of the first set were stirred at 25°C over different time intervals (10–180 min). In the other two sets, the solutions were stirred at 40 and 60°C respectively with the same previous conditions. The Cd(II) adsorption degree (R%) was determined using Eq. (2). The experimental adsorption data were used to plot the R% versus the contact time (t, min) at the fixed solution temperatures.The appropriate optimal time and temperatures for attaining the complete quantitative adsorption of Cd(II) were determined.

The adsorption capacity of cadmium by the adsorbent Q_m was calculated as the number of moles of adsorbed Cd(II) per gram of the adsorbent (11). The adsorption capacities Q_m of the adsorbents were determined experimentally under optimal conditions. For this purpose , a series of solutions were prepared with the same amount of the adsorbent (25 mg), γ-dinitrophenolas a third component (30 mg/ml) and increasing concentrations of the Cd(II)from 1 to 30 μg/ml. The systems were stirred with a magnetic stirrer (with 300rpm) at the optimal conditions predetermined. Then, the amount of the adsorbed element in each experiment was determined, and the dependence of the adsorption degree on the mass of the introduced element was constructed. The mass of the element limited in capacity for 25 mg of the specified adsorbent was determined by the inflection point of the curve.The equilibrium sorption capacity Q_m(mg/g), was calculated by Eq. (3) (12):

$$Q_{\max} = \frac{(C_0 - C_e)\, V}{w} \qquad (3)$$

whereC_0 and C_s are initial and equilibrium concentrations of Cd (II) in the solution µg/ml, respectively; *V* is the solution volume(L) and *w* is the adsorbent mass (g).

Selectivity test

The effect of various foreign ions was carried out under the preselected optimal conditions using the above – described protocol. A series of solutions were prepared with a fixed concentration of the element to be determined, fixed adsorbent and ligand masses. Different multiple mass amount of foreign ions with respect to Cd(II) ion amount was added individually to the above solutions as (1:0.1, 1:1, 1:10, 1:100, 1:500, 1:1000, 1:5000, and 1:10000), and the procedures for the determination of Cd (II) followed. We carried out series of experiments to improve the selectivity of Cd(II) adsorption with masking agents for foreign macro elements that exceed the possible ratios.

Desorption test

After preconcentration of Cd(II) ions on the PSAHB-NO_2 adsorbent, desorption of Cd(II) ions from the adsorbent was carried out by washing the concentrate on a paper filter to a beaker with 10 mL of varying concentrations of HCl and HNO_3 solutions consecutively (1M to 4M). Then, the system mixed using a magnetic stirrer for 1hour. The desorption degree of Cd (II)ions from the adsorbent was determined by a spectrophotometric method using the equation (4):

$$D,\% = \frac{C_d}{C_i} \times 100 \qquad (4)$$

Where C_d is concentration of desorbed Ni(II) in acidic solution and C_i is concentration of adsorbed Ni(II) onto adsorbent. All measurements of adsorption as well as desorption experiments were repeated three times. The shown values are averaged.

Results and Discussion

Calibration Graph and Analytical Characteristics

The Cd(II) adsorbs obeyed Beer's law over the range1-15µg/ml with a correlation coefficient of 0.999. The LOD (13) was calculated based on $3S_b / m$; where S_b is the standard deviation of the blank signal and *m* is the slope of the calibration curve after preconcentration, which was obtained to be0.8µg/ml. The straight-line equation was $y = 0.1017 * C_{Cd} + 0.0042$ and ε = 2.15 x 10^4.

The third component dose

Figure 2 shows that the effectiveness of adsorption of Cd(II) ions on PSAHB- NO_2 adsorbent increases rapidly with increasing amount of the γ-dinitrophenol(as third component) in adsorption system. The significant increasing in adsorption was observed when the amount of γ-dinitrophenol ligand was reached to 30 µg/ml. Any further addition of the γ-dinitrophenol did not cause anysignificant change in the

adsorption. From the results, it was shown that each 25 µg of element with 25 mg of adsorbent requires 30 µg/ml of the third component for quantitative sorption (R,%=100%) .

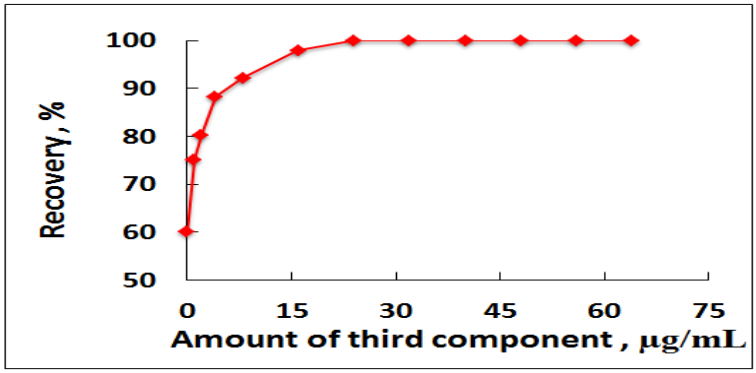

Figure 2: Effect of amount of γ-dinitrophenol as third component on R,% of 25 μg Cd ions [mass adorb.= 25 mg, *V* = 25 ml, pH 6, *t* = 100 min., T= 25°C

Effect of pH

Figure (3) shows the effect of the acidity of solution on the adsorption of Cd(II) ions by adsorbents 1–4 in the presence of γ-dinitrophenol. The values of pH_{50} for cadmium adsorption (Table 2) were determined graphically at R = 50% and *T*= 25 ± 2°C.

Table 2: Chemisorption of Cd ions in mixed –ligand complex adsorbents with the γ-Dinitrophenol ligand (T = 25 ± 2°C; µ = 1)

No.	Adsorbents	pH_{opt}	R, %	PH_{50}	t ,min	log β
1	PSAHB-H	7.5-8.5	100	4.7	15	8.33
2	PSAHB-Br	5.5-7.0	100	3.2	20	8.15
3	PSAHB-NO_2	4.0 -4.5	100	2.4	15	7.30
4	PSAHB- SO_3H	5.5-6.5	100	2.6	15	8.63

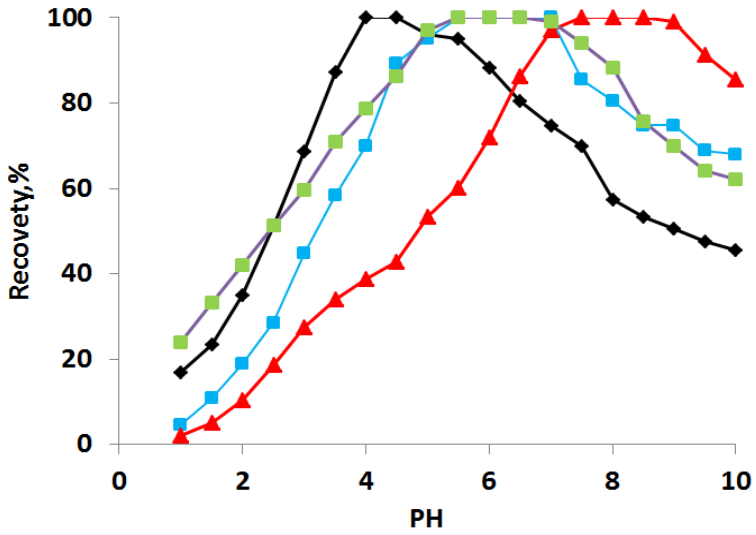

Figure 3: Effect of pH on Cd(II) adsorption by 1, 2, 3 and 4 adsorbents [25 mg of adsorbent, 25 µg of Cd(II), 30mg/g γ-Dinitrophenol Sample vol.=25 ml, t=25°C

Comparison of efficiency of α-dinitrophenoland γ-dinitrophenolligands

Based on the experimental data in Table (2), it was concluded that the polystyrene -(4- azo-1') -2'-hydroxyl -5'- nitrobenzene adsorbent (PSAHB- NO_2) interacted with Cd(II) ions in a more acidic region at pH_{50} 2.4 .Therefore, this adsorbent was used to compare the effect of addition of third components: α-dinitrophenol and γ-dinitrophenol. Thus, Table (3) shows the adsorption process of Cd(II) with α-dinitrophenol; the value of pH_{50} was 3 and pH_{opt} falls in the range of 5-5.5 (Figure 4), whereas with γ-dinitrophenol, the values of pH_{50} was 2.4 and pH_{opt} were 4-4.5.

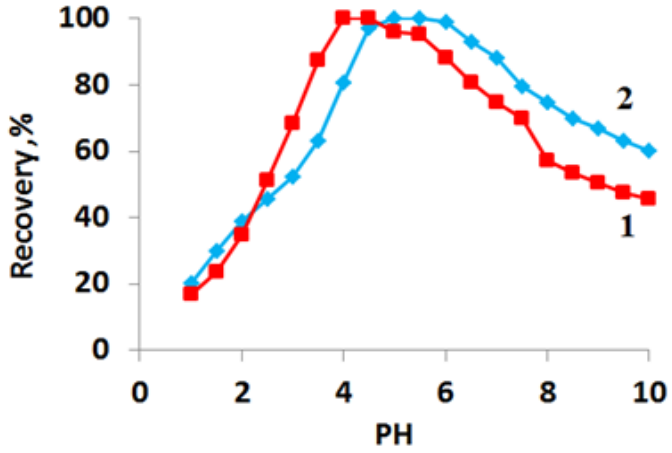

Figure 4: The effect of addition of a third component (1:γ-Dinitrophenol and 2: α-dinitrophenol) on the pH shift of Cd(II) adsorption with PSAHB-NO_2 adsorbent

The experimental data suggest that the adsorption of cadmium (II) in a more acidic region occurred upon the addition of the third componentγ-dinitrophenolto the system. This was due to a PH shift to a more acidic region because of the electronic substituent effects of the nitro groups (NO_2) on the dissociation constant of the phenolic group (-OH). The substituent nitrogroups (2 NO_2) in *o,m*-substituted phenol, in comparison with the o,*p*-positions, sharply shift $PH_{50}$of sorption to a more acidic region. The introduction of more activated electron-withdrawing substituents into the adsorbent structure leads to shifting inPH_{50} of the adsorption of the Cd(II)ions to a more acidic region. As a result, the strength of the bond in the complex" adsorbent-Cd (II) –*o,m*-substituted phenol" increases and the coordination number of the Cd was realized.

Table 3: Physicochemical properties of the mixed-ligand complexes on Cd(II) adsorption with PSAHB-NO_2 and the third component

The third component	pH opt	pH_{50}	R, %	Q m mg / g	t, min.
α-dinitrophenol	5.0 - 5.5	3.0	100	15.03	15
γ-dinitrophenol	4.0 - 4.5	2.4	100	13.80	15

Effect of time and temperature

The effect of time and temperature on the adsorption degree of Cd (II) (Recovery,%) in the ternary system with presence of the γ-dinitrophenollig are shown on Figure (5).

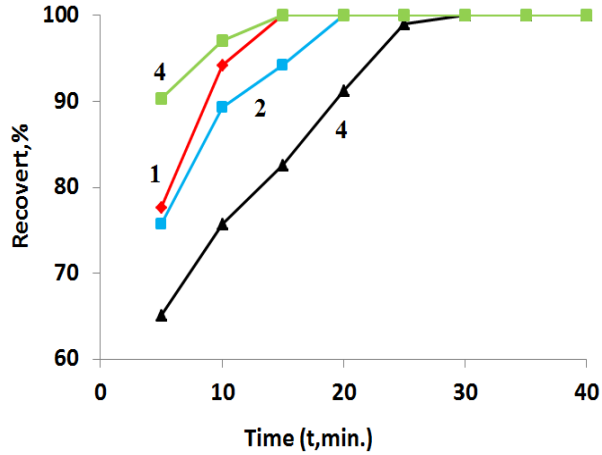

Figure 5: Effect of contact time on Cd(II) adsorption by polymeric adsorbents 1,2,3 and 4 at 25°C .

The best kinetic characteristics at *T*= 288 *K* were with PSAHB-NO_2 adsorbent, because quantitative adsorption (R = 100%) occurred at 15 min (Table II). Increasing the temperature to 60°C reduces the sorption time (by 5 - 10 min), but leads to partial destruction of the complexes and a decrease in the R% value from 100% to 86%.

Adsorption capacity of adsorbents (Q_{max})

The adsorption capacity of the adsorbents (Q_{max}) of each Cd(II) ions – a third component –an adsorbent system was determined experimentally as the amount of adsorbed Cd(II) mg per gram of the adsorbent at optimal sorption conditions. The Q_{max} values presented in Table (4) and Figure (6) show that nitro-substituted adsorbent is more selective and provides quantitative adsorption. The found sorption capacity of this adsorbent for the Cd (II) ions was 9.47 mg of Cd (II) per gram of the adsorbent.

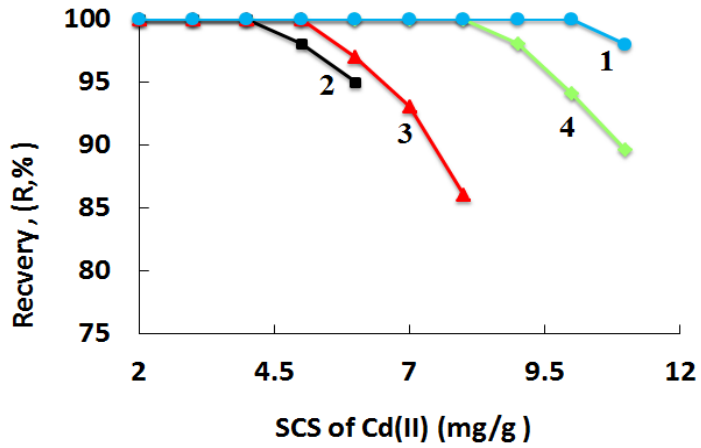

Figure 6: Sorption capacity of Cd(II) ions of 1- 4 adsorbents in presence γ-Dinitrophenol ligand

The values of Q_{max} used in calculating the required mass of adsorbent, applied to the analysis of Cd(II) in artificial and natural objects. Table (4) shows comparison of adsorption capacity of our chelating adsorbents with and without γ-dinitrophenol ligand. The data presented in Table (4) reveal that, generally, the chelating adsorbents with the added ligand have a good efficiency in metal ion adsorption more than the same adsorbents without this ligand.

Table 4: Comparison of Q_m adsorbents under study with and without the γ-dinitrophenol ligand as third component

No.	Adsorbents	Adsorption capacity Q_m (mg/g)	
		with γ-dinitrophenol (this work)	Without γ-dinitrophenol (previous work)
1	PSAHB-H	4.25	2.57
2	PSAHB-Br	3.42	2.06
3	PSAHB-NO_2	9.47	6.66
4	PSAHB- SO_3H	7.60	6.04

Selectivity studies

The effect of foreign cations on the adsorption of Cd(II) ions was studied by adsorbents, and was found out that the polystyrene-(4-azo-1')-2'-hydroxy-5'-nitobenzene has high selectivity for Cd(II) ions in the presence of γ-dinitrophenol even

in the presence of high concentration of foreign ions. The results presented in Table (5) indicate high possible ratios of the foreign cations do not interfere with the determination. The high selectivity of this mixed-ligand complex has allowed us to develop rapid procedures for determining of Cd(II) in artificial and environmental objects.

Table 5: Permissible ratios of interfering ions indetermination of Cd(II) with mixed- ligand complexes

Cations	Possible ratio	Recovery/%
N^+ , K^+	5 x 10^4	100.3±1.81
Ca^{2+} , Mg^{2+} , Fe^{2+}, Ba^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sr^{2+}	5 x 10^3	99.3±2.1
Al^{3+}, Mn^{2+} , Fe^{3+} ,, Ni^{2+}, Cr^{+3}	5 x 10^3	98.8±0.5

The possibility of increasing the selectivity of Cd(II) adsorption was studied with masking agents for foreign macro elements in amounts higher than permissible ones. Masking agents chosen with large amounts of Fe^{3+}, Al^{3+}(each 5 mg), Cr^{3+}, $Ca^{2+}$and Mg^{2+} (each 6 mg). It was found that adding 0.5 g of sulfosalicylic acid agent individually to Fe^{3+}, $Al^{3+}$and 0.5 g of sodium dihydrogen phosphate agent to Cr^{3+}, $Ca^{2+}$and Mg^2 solutions made it possible for quantitatively preconcentrate the trace amounts of Cd (II) ions in the presence of these foreign ions.

Desorption and regeneration studies

The results desorption of Cd (II) from the adsorbent, listed in Table (6), indicate that HCl acids is weak desorbing agent. This is evidence of a strong bond between the adsorbate and adsorbent. Only when HNO_3 acid was used; a significant increase in the degree of desorption was realized. It was found that as the concentration of the HNO_3 used as increased, there was an improvement in the effectiveness of the adsorbent regeneration process.

Table 6: Desorption of Cd (II) ions from adsorbents and γ-dinitrophenol ligand

Acid	M	V,ml	The degree of desorption of Cd(ll) (%)			
			1	2	3	4
HCI	1M	5	65	60	61	*66*
		10	88	81	80	85
	2M	10	95	85	84	92
HNO_3	1M	5	96	87	84	96
		10	98	90	86	99
	2M	5	100	95	90	100
		10	100	100	100	100

The mechanism of desorption is based on the exchange of hydrogen ions H^+ with the adsorbed metal ions. The cyclic adsorption–desorption studies were performed to estimate the ability of regeneration with results presented in Figure (7). The degree of

adsorption was shown consistently at a level > 90% for each cycle after desorption with 12 cycles. The results proved the high regeneration ability of the adsorbent.

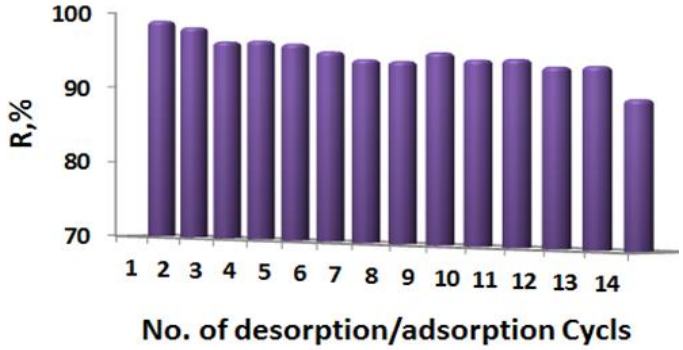

Figure 7: Adsorption–desorption cycles of adsorption of Cd on PSAH-NO_2adsorbent and γ-dinitroaniline

Predicted structure of the formed complex

The number of liberated protons (n) during the adsorption of Cd (II) with presence of α-dinitrophenol was determined by the Astakhov method (14). The number of liberated protons was calculated from the slope of the $\log \frac{R}{(100-R)} - pH$ curve.

It was found one proton to be displaced for a Cd(II) ion in this system, where the slope of the curve = 1; therefore, the liberated protons n = $1H^+$. The mechanism of cadmium adsorption in this system is defined inEq.4, 5.

$$2HR + Cd^{+2} \rightleftharpoons H^+ + CdH(R)_2^+ \qquad (4)$$

$$CdH(R)_2^+ \rightleftharpoons CdR + H^+ \qquad (5)$$

Where H_2R refers to the chelating groups in the adsorbent and the added ligand and Cd refers to the complex adsorbent formed. Based on the experimental results, we can represent a fragment of the likely structure of the mixed- ligand complex with α-dinitrophenol (Figuer 8).This structure indicates that the coordination bonds of Cd(II) formed by a nitrogen atom at -N=N- azo group that has a basicity greater than a nitrogen located closer to the hydroxyl group . The result is a six-membered ring, which is more strong than a five-membered ring (15). This structure indicates that Cd has two valence bonds with atoms ofoxygen (-O-)and oxygen of (-OH-) in α-dinitrophenoland one coordination bond with the nitrogen atom of the azo group. The net positive charge of the Cd^{+2} is balanced by the anions present in the solution.

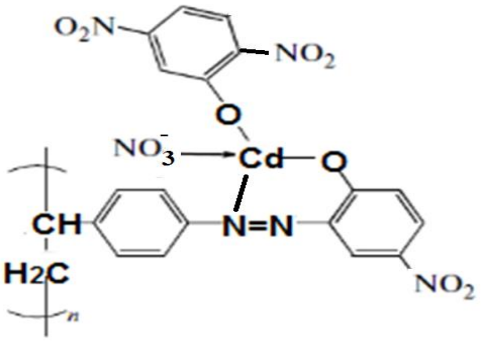

Figure 8. Suggested structure of the formed ternary complex (PSAHB-NO_2-Cd(II)-γ-dinitroaniline)

Conclusion

In current results, it was found that adsorbent PSAHB-NO_2in presence ofα-dinitrophenol is most promising for extraction and preconcentration of Cd (II) from artificial and natural objects .They have a higher adsorption capacity (9.47 mg/g) and the best kinetic parameters; at 25°C, 100% recovery reached in 15 min with high selectivity. The method can be used for cadmium determination in real industrial, geological and industrial materials. Desorption tests confirmed the possibility of reusing the adsorbent as an effective adsorbent of environmentally harmful metals. Hence, it is concluded that this chelating adsorbent with α-dinitrophenollig and are durable adsorbents in metal ions removal from their solutions.

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دراسة تحليلية للتأثير التعقيدي لأيونات الكادميوم الثنائي مع بوليسترين المرتبط بمجموعة وظيفية في وجود مكون ثالث من الفا وجاما نيتروفينول في المحاليل المائية

بدر اسماعيل عبد الرزاق طالب*

علي سعد الوصابي**

المُلَخَّصُ

الدراسة الحالية طريقة، انتقائية، وحساسة، وموثوقة في الاسترداد والتعيين الطيفي لعياثر ايونات الكادميوم الثنائي في المحاليل المائية، تستند هذه الطريقة لتكون نظام تعقيدي ثلاثي المكون من ايون الفلز ومخلوط ليجاندي. ان تأثير إضافة ليجاندات الفا وجاما نيتروفينول على معقد ايون الكادميوم الثنائي بوجود ليجاند بوليسترين المرتبط بمجموعة وظيفية في المحاليل المائية تم بحثها .تم تعيين البارمترات المتضمنة،قيمة الدالة الحامضية المثلى لاسترداد أعلى قيمة من الايون، الدالة الحامضية عند استرداد 50% من الايون، الزمن و درجة الحرارة المثلى، سعة الامتزاز. تم تعيين ثابت الاستقرار للمعقدات بالإضافة إلى الامتزاز الانتقائي للأيون وكذلك اقتراح تركيب المعقد المتكون.

*أستاذ الكيمياء التحليلية -كلية التربية- جامعة الحديدة- اليمن

**قسم علوم الصيدلة-كلية الصيدلة-جامعة العلوم والتكنولوجيا- اليمن

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