

# An Analytical Study of Complexation Effect of Cd(II) Ion with Polystyrene Bonded Functional Group in the Presence of Third Component $\gamma$ -Dinitrophenol and $\alpha$ -Dinitrophenol in Aqueous Solutions

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## 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 (complexing adsorbent-Cd(II) ions-  $\alpha$ - and  $\gamma$ -dinitrophenol) system. The effect of adding  $\alpha$ - and  $\gamma$ -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<sub>opt</sub>), the half-adsorption pH value (pH<sub>50</sub>), time (t) and temperature (T), the adsorption capacity ( $q_m$ ), the stability constant of the complexation ( $\log\beta$ ) 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:** Cadmium ions, Chelating group, Desorption and Adsorption, Efficiency and Selectivity, Polystyrene-azo-phenol,  $\alpha$ - and  $\gamma$ -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<sub>1</sub>-M<sup>+n</sup>- ligand<sub>2</sub>) 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).

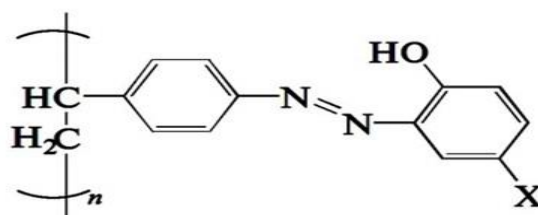
In these systems, the coordination capacity of a multi-charged cation is highest or complete to exclude the occurrence of masking, hydrolysis and solvolysis reactions, which result in a partial weakening of bonds in the complex and in a decrease in its stability (7, 8). Heretofore, we previously studied 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<sub>2</sub>, SO<sub>3</sub>H, COOH, CH<sub>3</sub> and NO<sub>2</sub>.

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 - $\alpha$ - and  $\gamma$ -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<sub>2</sub>,COOH,NH<sub>2</sub> or SO<sub>3</sub>H

**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 <sub>2</sub>    |
| 4   | Polystyrene(4-azo-1')-2'-hydroxy-5'-sulfo benzene | PSAHB- SO <sub>3</sub> H |

Cadmium (II) stock solutions were 1 mg.L<sup>-1</sup> (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  $\gamma$ -Dinitrophenol and  $\alpha$ -Dinitrophenol were Sigma-Aldrich (99.99%) with a concentration of 25 $\mu$ g/mL, (it was experimentally determined). A 200 / 0.0001g 0.1mg digital analytical balance TOPLAB India, a 781 pH/Ion meter with accuracy  $\pm 0.05$ pH, 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 with 15 standards in the range 1 - 15 $\mu$ g/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. 25 $\mu$ g) and 25 mg of adsorbent in 25 mL of aqueous solution, and variable multiple amounts of a third component ranging from 0 to 100 $\mu$ g/mL with respect to the element. Optimal pH values of Cd (II) adsorption pH<sub>opt</sub> 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  $\mu$ g of Cd(II)(C<sub>0</sub>) and 30  $\mu$ g/mL  $\gamma$ -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  $\mu\text{m}$ . The absorbance (A) of Cd(II) in the filtrate determined by a UV-Vis spectrophotometry with xylenol orange reagent (pH 6.2,  $\lambda_{\text{max}} = 580 \text{ nm}$ ,  $I = 1 \text{ cm}$ ) , 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):

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

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

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

These data used to create the graphs of R(%)versus solution's pH . From these graphs, the  $\text{pH}_{\text{opt}}$  corresponded to the highest R% and the values of  $\text{pH}_{50}$  at  $R = 50\%$  were determined graphically. According to the observed data, we determine the best adsorbent with  $\alpha$ - and  $\gamma$ -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  $\mu\text{g}$  of Cd (II), 25 mg of a adsorbent and 30 $\mu\text{g}$  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 ),  $\gamma$ -dinitrophenolas a third component (30 mg/ml) and increasing concentrations of the Cd(II)from 1 to 30  $\mu\text{g/ml}$ . 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  $Q_m(\text{mg/g})$ , was calculated by Eq. (3) (12):

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

where  $C_0$  and  $C_s$  are initial and equilibrium concentrations of Cd (II) in the solution  $\mu\text{g/ml}$ , 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- $\text{NO}_2$  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  $\text{HNO}_3$  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):

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

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

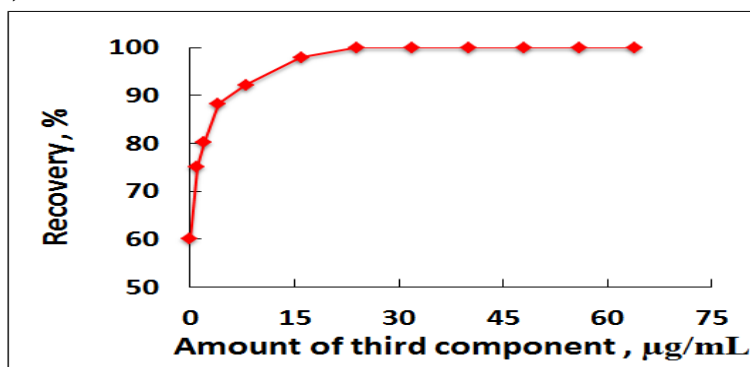
### Calibration Graph and Analytical Characteristics

The Cd(II) adsorbs obeyed Beer's law over the range 1-15 $\mu\text{g/ml}$  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 be 0.8 $\mu\text{g/ml}$ . The straight-line equation was  $y = 0.1017 * C_{Cd} + 0.0042$  and  $\varepsilon = 2.15 \times 10^4$ .

### The third component dose

Figure 2 shows that the effectiveness of adsorption of Cd(II) ions on PSAHB-  $\text{NO}_2$  adsorbent increases rapidly with increasing amount of the  $\gamma$ -dinitrophenol(as third component) in adsorption system. The significant increasing in adsorption was observed when the amount of  $\gamma$ -dinitrophenol ligand was reached to 30  $\mu\text{g/ml}$ . Any further addition of the  $\gamma$ -dinitrophenol did not cause any significant change in the

adsorption. From the results, it was shown that each 25  $\mu\text{g}$  of element with 25 mg of adsorbent requires 30  $\mu\text{g}/\text{mL}$  of the third component for quantitative sorption ( $R, \%=100\%$ ).



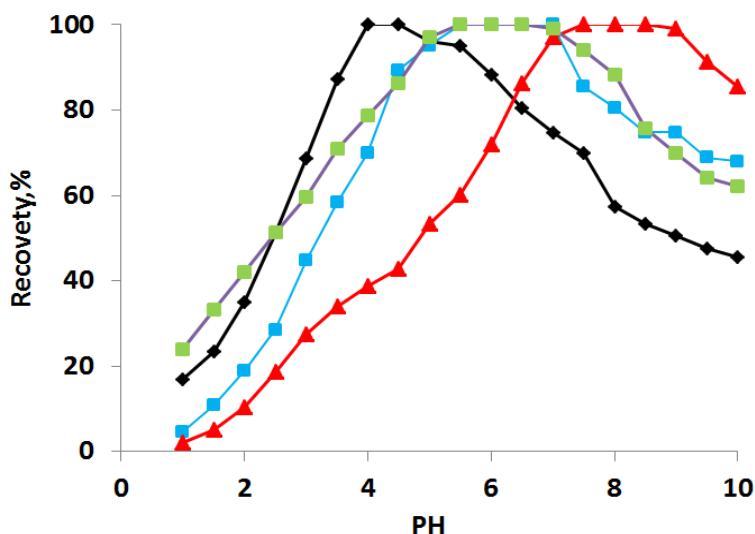
**Figure 2:** Effect of amount of  $\gamma$ -dinitrophenol as third component on  $R, \%$  of 25  $\mu\text{g}$  Cd ions [mass adsorb. = 25 mg,  $V = 25$  ml, pH 6,  $t = 100$  min.,  $T = 25^\circ\text{C}$ ]

### 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  $\gamma$ -dinitrophenol. The values of  $\text{pH}_{50}$  for cadmium adsorption (Table 2) were determined graphically at  $R = 50\%$  and  $T = 25 \pm 2^\circ\text{C}$ .

**Table 2:** Chemisorption of Cd ions in mixed –ligand complex adsorbents with the  $\gamma$ -Dinitrophenol ligand ( $T = 25 \pm 2^\circ\text{C}$ ;  $\mu = 1$ )

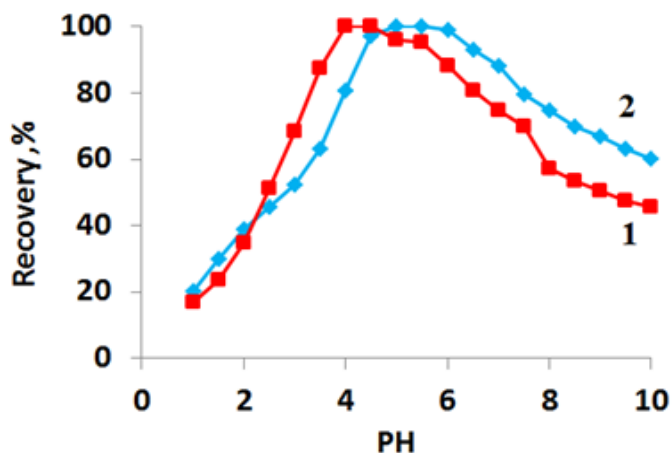
| No. | Adsorbents                   | $\text{pH}_{\text{opt}}$ | $R, \%$ | $\text{PH}_{50}$ | $t, \text{min}$ | $\log \beta$ |
|-----|------------------------------|--------------------------|---------|------------------|-----------------|--------------|
| 1   | PSAHB-H                      | 7.5-8.5                  | 100     | 4.7              | 15              | 8.33         |
| 2   | PSAHB-Br                     | 5.5-7.0                  | 100     | 3.2              | 20              | 8.15         |
| 3   | PSAHB- $\text{NO}_2$         | 4.0 -4.5                 | 100     | 2.4              | 15              | 7.30         |
| 4   | PSAHB- $\text{SO}_3\text{H}$ | 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  $\mu$ g of Cd(II), 30mg/g  $\gamma$ -Dinitrophenol Sample vol.=25 ml, t=25°C

### Comparison of efficiency of $\alpha$ -dinitrophenol and $\gamma$ -dinitrophenol ligands

Based on the experimental data in Table (2), it was concluded that the polystyrene -(4- azo-1') -2'-hydroxyl -5'- nitrobenzene adsorbent (PSAHB- NO<sub>2</sub>) interacted with Cd(II) ions in a more acidic region at pH<sub>50</sub> 2.4 .Therefore, this adsorbent was used to compare the effect of addition of third components:  $\alpha$ -dinitrophenol and  $\gamma$ -dinitrophenol. Thus, Table (3) shows the adsorption process of Cd(II) with  $\alpha$ -dinitrophenol; the value of pH<sub>50</sub> was 3 and pH<sub>opt</sub> falls in the range of 5-5.5 (Figure 4), whereas with  $\gamma$ -dinitrophenol, the values of pH<sub>50</sub> was 2.4 and pH<sub>opt</sub> were 4-4.5.



**Figure 4:** The effect of addition of a third component (1: $\gamma$ -Dinitrophenol and 2:  $\alpha$ -dinitrophenol) on the pH shift of Cd(II) adsorption with PSAHB-NO<sub>2</sub> adsorbent

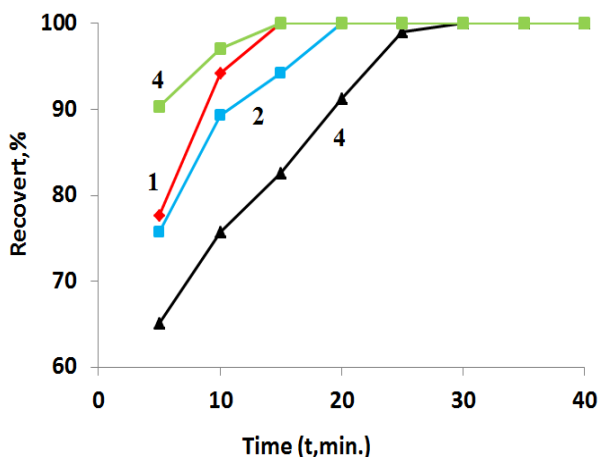
The experimental data suggest that the adsorption of cadmium (II) in a more acidic region occurred upon the addition of the third component  $\gamma$ -dinitrophenol to the system. This was due to a PH shift to a more acidic region because of the electronic substituent effects of the nitro groups ( $\text{NO}_2$ ) on the dissociation constant of the phenolic group ( $-\text{OH}$ ). The substituent nitro groups ( $2 \text{ NO}_2$ ) in  $o,m$ -substituted phenol, in comparison with the  $o,p$ -positions, sharply shift  $\text{PH}_{50}$  of sorption to a more acidic region. The introduction of more activated electron-withdrawing substituents into the adsorbent structure leads to shifting in  $\text{PH}_{50}$  of the adsorption of the  $\text{Cd(II)}$  ions to a more acidic region. As a result, the strength of the bond in the complex "adsorbent- $\text{Cd(II)}$  -  $o,m$ -substituted phenol" increases and the coordination number of the Cd was realized.

**Table 3:** Physicochemical properties of the mixed-ligand complexes on  $\text{Cd(II)}$  adsorption with PSAHB- $\text{NO}_2$  and the third component

| The third component     | $\text{pH}_{\text{opt}}$ | $\text{pH}_{50}$ | R, % | $Q_m \text{ mg / g}$ | t, min. |
|-------------------------|--------------------------|------------------|------|----------------------|---------|
| $\alpha$ -dinitrophenol | 5.0 - 5.5                | 3.0              | 100  | 15.03                | 15      |
| $\gamma$ -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  $\text{Cd(II)}$  (Recovery, %) in the ternary system with presence of the  $\gamma$ -dinitrophenol are shown on Figure (5).

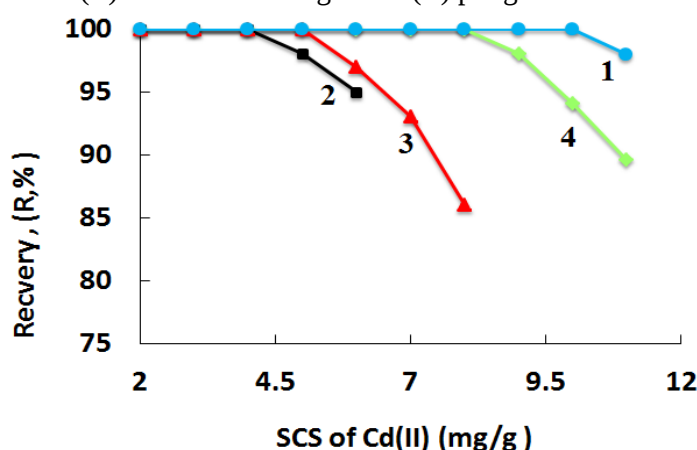


**Figure 5:** Effect of contact time on  $\text{Cd(II)}$  adsorption by polymeric adsorbents 1, 2, 3 and 4 at  $25^\circ\text{C}$ .

The best kinetic characteristics at  $T = 288 \text{ K}$  were with PSAHB- $\text{NO}_2$  adsorbent, because quantitative adsorption ( $R = 100\%$ ) occurred at 15 min (Table II). Increasing the temperature to  $60^\circ\text{C}$  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  $\gamma$ -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  $\gamma$ -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  $\gamma$ -dinitrophenol ligand as third component

| No. | Adsorbents               | Adsorption capacity $Q_m$ (mg/g)         |                                                 |
|-----|--------------------------|------------------------------------------|-------------------------------------------------|
|     |                          | with $\gamma$ -dinitrophenol (this work) | Without $\gamma$ -dinitrophenol (previous work) |
| 1   | PSAHB-H                  | 4.25                                     | 2.57                                            |
| 2   | PSAHB-Br                 | 3.42                                     | 2.06                                            |
| 3   | PSAHB-NO <sub>2</sub>    | 9.47                                     | 6.66                                            |
| 4   | PSAHB- SO <sub>3</sub> H | 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'-nitrobenzene has high selectivity for Cd(II) ions in the presence of  $\gamma$ -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/%       |
|-----------------------------------------------------------------------------------------------|-----------------|------------------|
| $N^+$ , $K^+$                                                                                 | $5 \times 10^4$ | $100.3 \pm 1.81$ |
| $Ca^{2+}$ , $Mg^{2+}$ , $Fe^{2+}$ , $Ba^{2+}$ , $Cu^{2+}$ , $Zn^{2+}$ , $Pb^{2+}$ , $Sr^{2+}$ | $5 \times 10^3$ | $99.3 \pm 2.1$   |
| $Al^{3+}$ , $Mn^{2+}$ , $Fe^{3+}$ , $Ni^{2+}$ , $Cr^{3+}$                                     | $5 \times 10^3$ | $98.8 \pm 0.5$   |

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

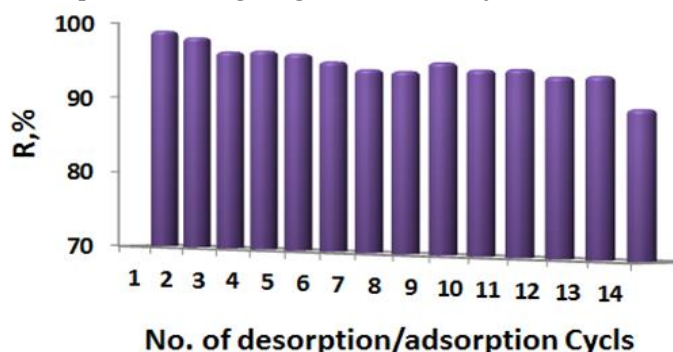
The results desorption of Cd (II) from the adsorbent, listed in Table (6), indicate that HCl acids is weak desorbing agent. This is evidence of a strong bond between the adsorbate and adsorbent. Only when  $HNO_3$  acid was used; a significant increase in the degree of desorption was realized. It was 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  $\gamma$ -dinitrophenol ligand

| Acid             | M  | V,ml | The degree of desorption of Cd(II) (%) |     |     |     |
|------------------|----|------|----------------------------------------|-----|-----|-----|
|                  |    |      | 1                                      | 2   | 3   | 4   |
| HCl              | 1M | 5    | 65                                     | 60  | 61  | 66  |
|                  |    | 10   | 88                                     | 81  | 80  | 85  |
|                  | 2M | 10   | 95                                     | 85  | 84  | 92  |
|                  |    | 5    | 96                                     | 87  | 84  | 96  |
| HNO <sub>3</sub> | 1M | 10   | 98                                     | 90  | 86  | 99  |
|                  |    | 5    | 100                                    | 95  | 90  | 100 |
|                  | 2M | 10   | 100                                    | 100 | 100 | 100 |
|                  |    | 5    | 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.

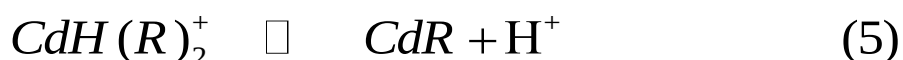
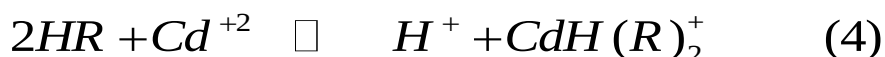


**Figure 7:** Adsorption–desorption cycles of adsorption of Cd on PSAH-NO<sub>2</sub> adsorbent and  $\gamma$ -dinitroaniline

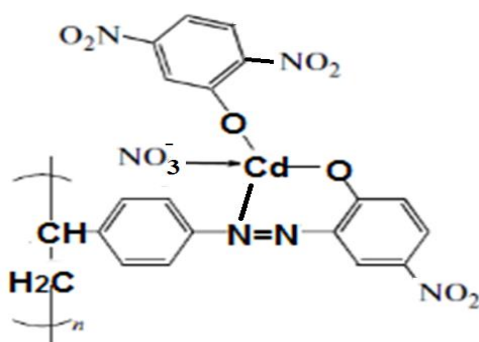
### Predicted structure of the formed complex

The number of liberated protons (n) during the adsorption of Cd (II) with presence of  $\alpha$ -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 in Eq.4, 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  $\alpha$ -dinitrophenol (Figure 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 of oxygen (  $-O-$  )and oxygen of ( $-OH-$ ) in  $\alpha$ -dinitrophenol and 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<sub>2</sub>-Cd(II)-γ-dinitroaniline)

## Conclusion

In current results, it was found that adsorbent PSAHB-NO<sub>2</sub> in presence of α-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-dinitrophenol 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

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## المُلخَص

الدراسة الحالية طريقة، انتقائية، وحساسة، وموثوقة في الاسترداد والتعيين الطيفي لعيائر 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.

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