Analytical Characterization of Polystyrene Polymer Adsorbents functionalized with Azo-phenolic Chelating Groups and their Use for Preconcentration and Extraction of Trace Amount of Nickel Ions in Aqueous Solutions

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ABSTRACT

The modern instrumental analysis methods do not always allow direct determination of trace amounts of elements due to influence of the matrix composition of the sample. New complex adsorbents based on aminopolystyrene functionalized with azo-phenolic chelating groups applied for preconcentration of Ni(II) ions in its aqueous solutions. Optimal parameters affecting *on the adsorption efficiency determined. The best adsorbent selected for subsequent tests. Dissociation constants of an adsorbent determined. The adsorption isotherm evaluated and the kinetics data analyzed. Thermodynamic parameters studied. The structure of the complex formation suggested. We found out that PSAPH-SO₃H adsorbent has the best kinetic characteristics for nickel adsorption; at 25℃, 98.9% recovery achieved in 30 min. The Langmuir isotherm gives better fit to adsorption isotherm results. The adsorption of Ni(II) ions obeyed to pseudo-second order model. The thermodynamic parameters clarify that the spontaneous and endothermic nature of adsorption. The ionization stage of -N=N-group=4.27, of SO_3H group=6.36 and of -OH group=7.95. The results can be used in the complex compound chemistry for the development of procedures for treatment of Ni^{2+} ions from naturally-occurring and industrial materials.*

Keywords: Adsorption; Chelating groups; Dissociation constants

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INTRODUCTION

The pollution of heavy metals has attained worldwide attention due to their toxicity, non-biodegradable nature, and accumulation in the living organisms. The treatment of wastewater contaminated by heavy metals is an important environmental and public health concern. Nickel selected as adsorbate because its compounds have widespread applications in many industrial processes [1]. When the concentration is exceeded above the safe limit (0.15 mg/L),

the nickel exhibit toxic properties, a non-biodegradable character and causing several diseases [2-5]. Nowadays, various methods achievable for removal of heavy metals from its aqueous solutions; including membrane systems, electro-deposition, chemical precipitation and ion exchange process [6-9]. Generally, they are very expensive or ineffective particularly when the metal concentration is less than 100 μg/ml [10]. The modern instrumental analysis methods do not always allow direct determination of trace amounts of elements due to influence of the matrix composition of the sample or the low concentrations of the elements being determined. However, adsorption of heavy metallic ions by chelating polymer adsorbents can be respected as the most common methods for the removal of hazard heavy metals from the aqueous solutions by cause of their lower costs, high removal efficiency,, robustness, high efficiency and biodegradability, especially for metal ions at levels 10^{-5}-10^{-8}% [8,10,11]. Using of chelating polymer adsorbents for removal of metal ions from aqueous solution has been widely studied [12-18]. The important characteristic of these adsorbents depends on the active chelating positions (groups) such as amidoxime, iminoacetate, dithiocarbamate, aminoazobenzenesulfamido and amino which have ability of chelating about metallic ions during complication processes [15-17].

A new class of chelating polymer adsorbents have been synthesized based on amino-polystyrene functionalized with chelating azo-2'-hdroxy benzene and p-substituents of various electronic natures with respect to the hydroxyl group which are insoluble in water, acids, alkalis, and organic solvents and undergo regeneration 9-11 working chemisorption cycles [18], some of these adsorbents shown in Table 1. The objective of this work to study the potential of polystyrene azo phenol derivatives to remove Ni(II) ions from aqueous solutions under various conditions. The effect of process parameters such as time and temperature, initial amount of Ni(II) ions, adsorbent dosage and acidity on quantitative adsorption also investigated. The best polymer adsorbent was selected for subsequent tests. Dissociation constants of chelating groups of an adsorbent was invigilated. The Langmuir, Freundlich and Temkin models were employed for analysis of the adsorption equilibrium. The adsorption isotherms were found out using the Freundlich and Langmuir models. Kinetic and thermodynamic parameters also tested to identify the mechanisms of nickel ions adsorption process.

MATERIALS AND METHODS

Preparation of Reagents and Solutions

All chemicals used in the study were of analytical reagent grade. Nickel(II) stock solution of 1 mg/ml (1000 ppm) was prepared by dissolving the required weight of Ni $(NO_3)_2$.$6H_2O$ (Sigma-Aldrich) in double distilled water. Working standard solutions prepared by successive dilution of the stock solution. To create the required pH values, 0.1 M of HCl standard solution (pH: 1-2) and ammonia-acetate buffer solutions (pH: 3-10) were used. Dimethylglyoxime (H_2Dm), 1% solution in ethanol [19].

Characterization of Adsorbents

We applied polystyrene-azo-phenol derivatives to adsorb the trace amount of elements in the model aqueous solutions. The nomenclatures of these adsorbents presented in Table 1 and Figure 1. This class of adsorbents purchased from Central Chemical Laboratory of IGEM, Russian Academy of Sciences. The adsorbents synthesized according to procedures [20-23]. The synthesis included four successive stages : (a)Nitration of a polystyrene to polynitrostyrene ;(b) Reduction of this product to polyaminopolystyrene ; (c) Diazotization of the produced amino

group; (d) Azocoupling of the diazotized amino with monomeric organic reagents. The adsorbents were dark brown grains with 0.4-1.2 mm size and the pore size lies in the range of 0.01-0.1 μm, insoluble in water, acids, alkalis, and organic solvents and do not swell. The chelating polymer adsorbents were of chemically pure grade. The absorbents were ground in an agate mortar and bolted through a sieve of 200 meshes (0.074 nm) [22].

FT-IR Analysis

The FTIR of PSAHB-SO$_3$H adsorbent attained with Shimadzu 8601 PB in the 400-4000 cm^{-1} range in KBr phase. The IR spectrum of the PSAHB-SO$_3$H adsorbent as example shown in Figure 2. Analysis of the FT-IR spectrum of PSAHB-SO$_3$H adsorbent confirmed the presence of functional groups characteristic of adsorbent. Hydroxyl group was identified by the broad band attributed to stretching vibrations of O-H bonds in the range 3600-3100 cm^{-1}, while additionally ether groups were manifested by the band attributed to stretching vibrations of C-O bonds at 1100-1000 cm^{-1}, the signals at 1600 cm^{-1}, 1550 cm^{-1}, 1450 cm^{-1} associated with (phenyl); 1630 cm^{-1} (-N=N-); 3060 cm^{-1} (Ar-H) and signal at 1350 cm^{-1} associated with the stretching vibrations of C-OH groups in the structure of adsorbant. The presence of aliphatic structure is confirmed attributed to the stretching vibrations of C-H bonds in the range 2940-2850 cm^{-1}. The signal 710-680 cm^{-1} associated with deformation vibrations of C-C groups in the benzene ring. Thus, the IR spectrum of the adsorbent confirms the structure of adsorbants.
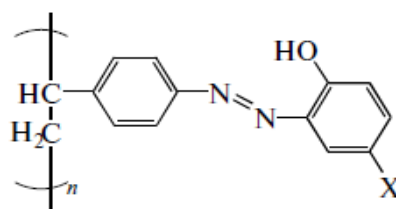

Figure 1. The structure of the adsorbents (PSAHB-X) where X: H, Br, NO$_2$, SO$_3$H, CH$_3$, COOH and NH$_2$

Table 1. Nomenclature of our complex polymer adsorbents under study

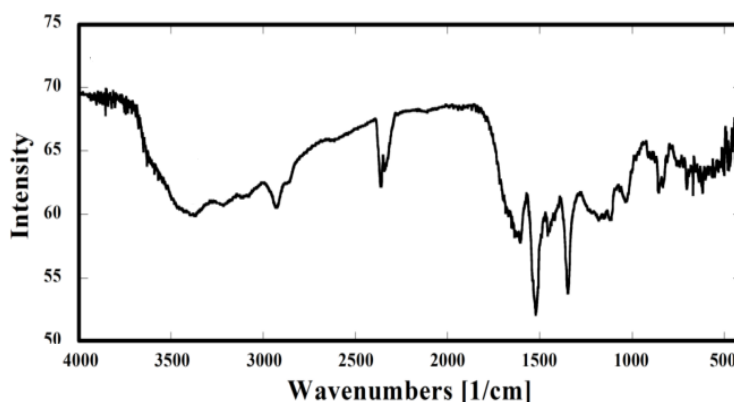| Name of Adsorbent	Abbreviation
Polystyrene(4-azo-1')-2'-hydroxy-5'-benzene	PSAHB-H
Polystyrene(4-azo-1')-2'-hydroxy-5'-chlorobenzene	PSAHB-Br
Polystyrene(4-azo-1')-2'-hydroxy-5'-nitrobenzene	PSAHB-NO2
Polystyrene(4-azo-1')-2'-hydroxy-5'-sulfobenzene	PSAHB-SO3 H

Figure 2. FTIR spectrum of PSAHB-SO$_3$H adsorbent

Batch Adsorption Studies

Effect of adsorbent dosage: Initial metal concentration25 μg in 25 ml solution, *T* 25°C, solution's pH ~5.5, contact time 90 min, adsorbent dosage 1, 5, 10, 20, 30, 40, 50 mg.

Effect of solution's pH: The optimum adsorption pH was determined experimentally from the plots of adsorption degree (R%) versus pH in range from 1 to 10 (Figure 3). For this purpose, several sets of samples were prepared, 40-mL of 20 weighing bottles were each charged with 20 mg of an adsorbent and 2 mL of a nickel(Ni) solution (10 μg/mL). Aqueous solutions of 0.1 M HCl and 0.1 M NaOH was added to adjust the solution's pH (1-10), then, the volume of mixture was brought to 20 mL. The bottles were covered and stirred at 300 rpm for 90 min at 25 °C. An adsorbent collected on a Blue Band filter. Nickel ions in the filtrate C_e determined photometrically with H_2Dm reagent at λ=445 on a spectrophotometer, LasanyLi-295 using of earlier constructed calibration curves. The adsorption degrees of nickel (R, %) at the created pH values calculated using eqn. (1).

$$R,\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are initial and equilibrium concentrations of Ni(II) in the solution. The equilibrium adsorption capacity q_e (mg/g), was calculated by eqn. (2) [24].

$$q_e = \frac{(C_0 - C_e)\, V}{w} \qquad (2)$$

where C_0 and C_e are initial and equilibrium concentrations of Ni(II) in the solution (mg/L) respectively. *V* is the solution volume (L) and *m* is the adsorbent mass (g).

Effect of contact time and temperature: To investigate the effect of contact time and solution temperature on adsorption process, we prepared several sets of 20 ml of solutions each containing 20 mg of a adsorbent and 20 μg of nickel and pH was adjusted with predetermined optimal acidity. The solutions of the first sets stirred at 25 °C for 5, 10, 20, 30, 40, 60, and 90 min. In the other sets, solutions stirred at 40 and 60°C respectively and stirred under the similar conditions for 5, 10, 15, 30, 40, and 60 min. The adsorption degrees (R%) of Ni(II) were estimated using eqn. (1). The data obtained in this way used to plot adsorption degree (R, %) as a function of contact time (t, min) at the specified solution temperatures (Figure 4). The optimal time and temperature used for subsequent quantitative adsorption of nickel ions.

Effect of initial concentration of Ni(II) on adoption: Experiments to studies the effect of initial concentration of Ni(II)ions on adsorption were performed with four sets of solutions (for the four adsorbents) with 20 mg of the adsorbent and amounts of Ni(II) increased from 0.01 to 1.5 mg and the optimal pH was adjusted with 20 mL volume. The mixtures magnetically stirred at the optimal pH, time and temperature. Then, each adsorbent filtered, and the amount of the adsorbed Ni(II) was determined according to eqn. (1). These data were used to plot C_e with q_e curve, where C_e is equilibrium concentrations of Ni(II) in the solution, in mg/L and q_e is the equilibrium concentration of nickel ions in the adsorbent phase, in mg/g (Figure 5).

Calculation of Acid-Base Dissociation Constants pK$_{ion}$

To determine dissociation constants (pK$_{ion}$) of a PSAHB-SO$_3$H adsorbent, it is necessary to determine the static capacity SCC$_{ion}$ and dissociation stages of chelating groups on adsorbent:

A) Determination of static capacity of chelating groups (SCC$_{ion}$): Total static capacity of chelating groups of PSAHB-SO$_3$H adsorbent SCC$_{tot}$ determined experimentally by the potentiometric back titration [18,25]. A 20 ml of 0.05 M NaOH solution added to a 0.1 g of adsorbent sample in H$^+$ form placed in a 40 ml weighing bottle. The covered bottles placed into a desiccator filled with CO$_2$-free nitrogen and after passing 24 h ,the remaining concentration of NaOH was titrated by 0.05 M HCl standard solution with phenolphthalein (Ph.ph) as indicator. The static capacity of chelating groups (mmol/g) calculated from eqn. (3):

$$SCC_{tot} = \frac{(M_1 - M_2) \times 20ml}{0.1g} \qquad (3)$$

where M_1 and M_2 are the first and final concentration of NaOH respectively.

B) Determination of dissociation stages of chelating functional groups: Dissociation constants of PSAHB-SO$_3$H adsorbent was determined from potentiometric titration data at a constant ionic strength of the solution. 0.1 g portions of adsorbent in the H$^+$ form in 40 ml bottles, 15 ml of 1 M NaCl solution was added to each bottle to create ionic strength μ=1, and the mixtures were allowed to stay for 90 min. Then, different amounts of a 0.02 M NaOH solution were added to the bottles. Therefore, the neutralization degrees of chelating groups of the adsorbent (Q) could be varied from 0 to value of total static capacity SCC $_{tot}$ Q determined as the ratio of the added NaOH amount in millimoles to SCC$_{tot}$ of acidic chelating groups in the adsorbent. The mixtures were allowed to stay in a desiccator filled with nitrogen for 24 h. Then, the pH of the mixtures recorded and the integral curve constructed by plotting $_{pH-Q}$ coordinate. These curve exhibit several stages which indicate presence of several dissimilar chelating groups in the adsorbent. For accurately determine the positions of the dissociation stages of chelating groups, the integral titration curve converted into the differential curve in the $\frac{\Delta pH}{\Delta Q} - Q$ coordinates. Therefore, based on the static capacity of the individual groups SSC $_{indi}$ in the adsorbent, the α values (is the degree of neutralization of protons of chelating groups of adsorbent) were calculated. the α values calculated for each stage as the ratio between the amount of NaOH added (*MV* mmol) and the total amount of functional groups of all types(SSC$_{ion}$), mmol in eqn. (7) per 0.1 g of adsorbent:

$$\alpha = \frac{(M \times V)}{SSC_{indi} \times m} \qquad (4)$$

Based on the α values obtained and the corresponding pH, we plotted the ($_{pH} - \log\frac{\alpha}{(1-\alpha)}$) coordinates, from which the pK$_{ion}$ values determined graphically for each chelating group in adsorbent and the slope of the linear dependence (*n*) was used to calculate pK$_{ion}$ experimentally by the modified Henderson-Hasselbalch equation eqn. (5).

$$pK_{ion} = pH - n.\log\frac{\alpha}{(1-\alpha)} \qquad (5)$$

RESULTS AND DISCUSSION

Calibration curve of nickel standard solutions was constructed (10 standards used in the range 0.02-30 μg/ml with R^2=0.999, the straight-line equation was: A=0.101C$_{Ni}$+0.0005, LOD was 0.133 μg/mL and ε$_{445}$=6.1 x 10^3 *L.mol^{-1}cm^{-1}*.

Effect of pH on Nickel Adsorption

Figure 3 displays the curve of (R, %) of Ni(II) versus pH values of solution for the adsorbents under study. From this a curve we derived pH $_{opt}$ corresponding to highest R% and tabulated in Table 2. The adsorption degree (R, %) of Ni(II) $\geq$ 95% were observed in the range of 3-7.5 pH. As shown in (Figure 3), at low pH values, the R% values are low due to the increasing in the positive charges (protons H^+) on the surface of polymer (active sites: $N=NH^+$, $C-OH_2^+$, leading up to electrostatic repulsion between the Ni^{2+} ions and these active sites on the adsorbent surface. The increasing of pH leads to the decreasing of electrostatic repulsion because of the reduction of the positively charged active positions on the adsorption surface, thus resulting in an increase in the adsorption of Ni^{2+} ions on the surface. In the basic solution(at pH higher than 7, the adsorbent surface becomes negatively charges, and the adsorption degrees (R%) of Ni^{2+} ions decreased with the precipitation of Ni^{2+} ions as nickel hydroxide. Hence, the 3-7 pH values were the optimum acidity PH $_{opt}$) designated for further experiments.
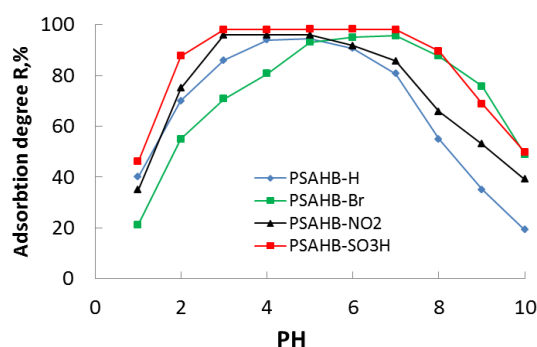

Figure 3. Adsorption degree (R%) of Ni(II) vs. pH [m $_{adsorb.}$=20 mg, m$_{Ni(II)}$=20 µg, T=25℃, Sample V=20 ml; pH=6 H$_2$Dm reagent (λ=445 nm)]

Table 2. Adsorption properties of Ni^{2+} ions on the adsorbents (n=3, P=95.5%)

Adsorbents	PH$_{opt}$	R, %	Contact time, min	The adsorption capacity mg/g
PSAHB-H	4.7-5.5	95	90	7.3
PSAHB-Br	4.5-7	97.3	60	9.2
PSAHB-NO2	3-5.5	98	40	11.7
PSAHB-SO3 H	3-7.5	98.9	30	14.2

Effect of Contact Time and Temperature

The optimal contact times of adsorbents were tabulated in Table 2. The best contact time with higher (R%) was with PSAHB-SO$_3$H adsorbent. Figure 4 illustrates how the contact time (t, min) and temperature of solution affect the adsorption degree of Ni(II) on PSAHB-SO$_3$H adsorbent at 20, 40 and 60℃. The (R%) increases with the increasing of contact time and temperature (Figure 4).
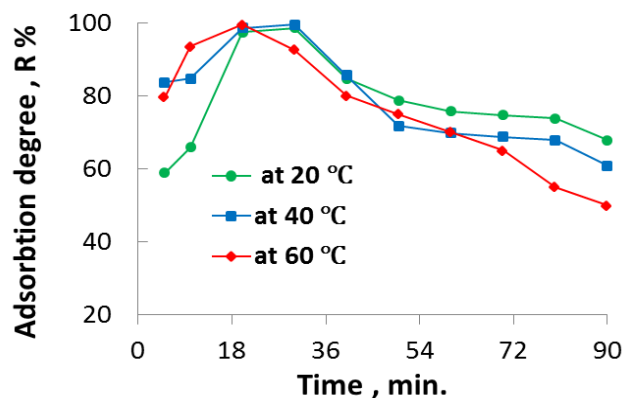
Figure 4. Effect of the contact time (t,min) on the R, % of Ni(II) on the PSAHB-SO₃H adsorbent at 20, 40 and 60℃. [m$_{adsorb.}$=20 mg, m$_{Ni(II)}$=20 μg, Sample V=20 ml; pH=6, H2Dm reagent (λ=445 nm, I=1 cm)]

Effect of Initial Concentration of Element

The influence of the first metal concentrations on equilibrium adsorption investigated and the obtained data illustrated in Figure 5. It is clear from the results that the adsorbed amount of Ni(II) ions onto chelating adsorbent increased as the first concentration of nickel ions increased. The increase reaches the plateau value (a bend at saturation point). The projection of this bend onto the y-axis matched the adsorption capacity of the Ni(II)-adsorbent system, the concentration of metal ions, after that, no longer affects the capacity of adsorption.

This confirms the existence of chemisorption rather than physical adsorption on the surface of adsorbents. Adsorption capacity of adsorbent is an important parameter for choosing the most effective adsorbents for preconcentration and separation of Ni(II) and other elements from their solution. The optimum adsorption capacities of adsorbents tabulated in Table 2 and show in Figure 5, the maximum adsorption capacities of adsorbents were in the order of PSAHB-SO₃ H>PSAHB-NO₂>PSAHB-Br>PSAHB-H. It is clear that PSAHB-SO₃ H adsorbent has thigh efficiency in preconcentration of nickel element in comparison with the others. A comparison of the Sorption capacity of our PSAHB-SO₃H adsorbent with different adsorbents in recently reported literatures presented in Table 3 [26-29].

Table 3. Comparison of maximum adsorption capacity of PSAHB-SO₃H adsorbent with of some other chelating adsorbents reported in literature for the adsorption of Ni(II)

Adsorbents	Sorption capacity (mg/g)	Conditions (Acidity &℃)	Ref.
Reduced size Dowex-50 (RDS-50)	13.9	pH=6, 25℃	12
Poly(hydroxyethyl methacrylate/maleamic acid)	13.75	pH=5.5, 25℃	13
Magnetic beads with amino groups	9.2	pH=4.5, 25℃	14
Cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base	22.4	pH=5, 30℃	17
Co3O4-containing resin with ethylenediamine chelating agent	15.09	pH=6, 28℃	26
Amidoximated-poly(ethylene terephthalate) fiber	5.6	pH=4, 25℃	27
Polystyrene azo-2'-hydroxy-5'-sulfobenzene	14.2	pH=6, 25℃	this work

The data indicates that the PSAHB-SO$_3$H adsorbent under study has good adsorption efficiency for nickel ions comparing to the previously reported adsorbents.
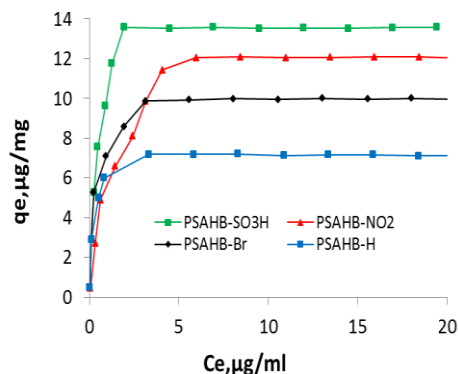

Figure 5. Effect of initial concentration of Ni(II) ions on the adsorption capacity of adsorbents [m $_{adsor.)}$=20 mg, V$_{solut.}$=20 ml, T=25°C ; pH=6.5, spectrophotometric H$_2$Dm reagent (λ=445 nm, I=1 cm]

Adsorption Isotherms

The adsorption isotherms used to illustrate the experimental data of adsorption. Different adsorption isotherms are obtainable. Langmuir, Freundlich and Temkin are most common used to explain the adsorption mechanism. Langmuir adsorption isotherm is model of monolayer adsorption onto a uniform surface of the active chelating sites of adsorbents. The linear form of Langmuir isotherm model is given by eqn. (6) [28]

$$\frac{C_e}{q_e} = \frac{1}{q_m . K_L} + \frac{C_e}{q_m} \qquad (6)$$

where C_e is the equilibrium concentration of metal in solution (mg/L), q_e is the equilibrium adsorption capacity on the adsorbent (mg/g), q_m and K_L are the Langmuir constants related to affinity towards to the adsorbent (the capacity of adsorption) energy of adsorption (L/mg), respectively. The parameters of Langmuir model were presenter in Figure 6 and Table 4.
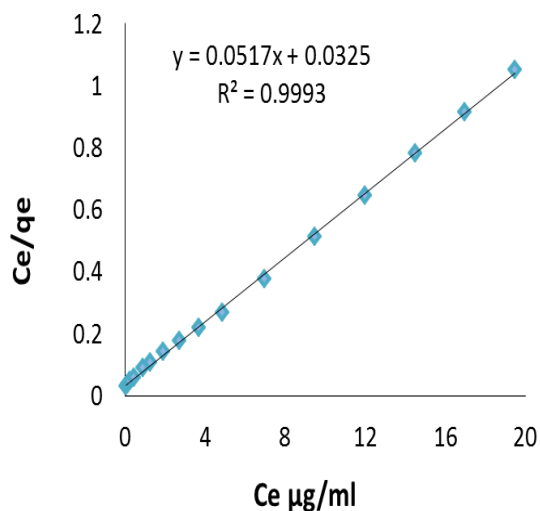

Figure 6. Linear Langmuir isotherm of the Ni(II) adsorption on PSAHB-SO$_3$H adsorbent. [m $_{adsorb.}$=25 mg, m $_{Ni(II)}$=25 µg, V $_{solut.}$=25 ml, T=25℃, pH=6, spectrophotometric H$_2$Dm reagent λ=445 nm, I=1 cm

Table 4. Langmuir, Freundlich and Temkin parameters of Ni(II) adsorption on PSAHB-SO₃H adsorbent from its aqueous solution

Isotherm model	Langmuir			Freundlich			Temkin		
Parameters	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n (L/g)	R^2	k_T (l/g)	B (mg/l)	R^2
Value	14.2	1.05	0.9993	7.57	2.24	0.87	5482	3	0.952

Maximum adsorption capacity (q_m) indicates monolayer coverage of the adsorbent with the adsorbed, and K_L indicates the enthalpy of the adsorption which differs with temperatures. The constant $q_m K_L$ is used as a distribution coefficient (K_d) in the low concentrations. The constant K_L corresponds to the affinity of the compound for the adsorbent. The values of q_m and K_L were tabulated in Table 4.

The Freundlich model is an empirical equation [29-31]. Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The equation commonly given by:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (7)$$

Where 1/n and K_F are the Freundlich constants, their values were calculated from the slope and intercept of the linear plot log q_e versus log C_e and reported in Table 4. The values of n>1, reflecting the favorable adsorption conditions [32].

The Temkin isotherm model represented by the eqn. (8) [33]:

$$q_e = B \log K_T + B \log C_e \qquad (8)$$

where B and K_T are constants of Temkin isotherm which are corresponding to the heat of adsorption (mg/l) and equilibrium binding constant(l/g). The constants B and K_T listed in Table 4. Comparison of the correlation coefficients values of three models lead to the adsorption Ni(II) onto PSAHB-SO₃H adsorbent is described well via the Langmuir isotherm than the Freundlich isotherm and Temkin isotherm.

Adsorption Kinetics

In order to investigate the kinetic mechanism, which controls the adsorption process, pseudo-first order kinetic model and pseudo-second order kinetic model, applied for the experimental data to explain the adsorption kinetics of nickel onto PSAHB-SO₃H at optimized conditions. These models used to characterize metallic ions adsorption onto chelating groups of adsorbents. The Lagergren pseudo-first-order kinetics model is one of the most broadly used to describe the adsorption of metal ions from aqueous solutions [34-36]. The linear form of pseudo-first-order equation expressed by eqn. (9).

$$\log(q - q_t) = \log q - (\frac{K_1}{2.303})\, t \qquad (9)$$

where q_t (mg/g) is the amount of Ni(II) ions adsorbed at time *t* and K_1 (tim^{-1}). The experimental values of the pseudo first-order rate constants tabulated in Table 5. The adsorption data have a poor correlation coefficient, which indicate that the adsorption of Ni ions on PSAHB-SO₃H does not obey completely the pseudo-first order adsorption kinetics.

The obtained experimental data modeled also using the pseudo-second order kinetic model. The linearity of pseudo-second-order kinetic model given by eqn. (10) [37]

$$\frac{t}{q_t} = \frac{1}{(K_e \cdot q_e^2)} + \frac{t}{q_e} \qquad (10)$$

where K_2 ($g \cdot mg^{-1} \min^{-1}$) is the pseudo-second order kinetic rate constant.. The parameters for this model show a great compliance with the pseudo second-order equation (Figure 7). The correlation coefficients of the second order kinetic given in Table 5 are higher than the results obtained from the first-order kinetics. Therefore, the adsorption behavior of Ni(II) onto chelating groups of PSAHB-SO$_3$H adsorbent follows the second-order kinetics.
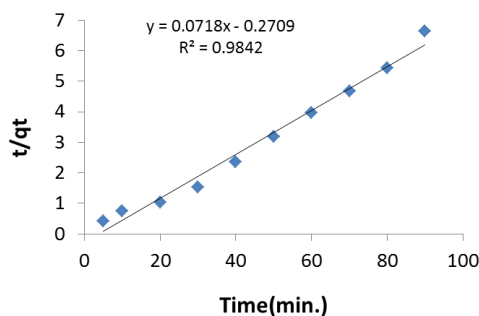

y = 0.0718x - 0.2709
R² = 0.9842

Figure 7 Pseudo-second order adsorption kinetics of nickel ions onto PSAHB-SO₃H

Table 5. First-order, second-order kinetic models and coefficients of determination for the adsorption of nickel(II) ions onto PSAHB-SO₃H adsorbent

Kinetic models		Pseudo-first-order			pseudo-second-order		
Parameters	**q_e (exp)**	**q_e (cal)**	**R^2**	**k_1 (1/min)**	**q_e (cal)**	**R^2**	**k_2 (1/min)**
values	14.2	13.8	0.875	-0.00507	13.93	0.984	-52.6

Conditions: initial Ni(II) concentration, 20 µg ; T=298 K; adsorbent amount; 20 mg, V $_{slout.}$, 20 ml; pH=6.5

Determination of Thermodynamic Parameters

Thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 of the adsorption process were calculated by carrying out the adsorption experiments at different temperatures (20, 40 and 60℃) with optimum conditions.

Free energy change of the adsorption ΔG^0 (J) was calculated by eqn. (11) [38]:

$$\Delta G^0 = RT\ln K_d \qquad (11)$$

where R is the ideal gas constant R=8.314 (J/mol. K), T is the absolute temperature (K), and K_d is equilibrium distribution coefficient for the adsorption process. K_d, was estimated by eqn. (12) [39].

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \qquad (12)$$

where C_0 and C_e are the amount of the initial and equilibrium concentration of Ni(II) (mg/L), *V* is the volume of the solution in (L) and *m* is the mass of the chelating adsorbent used in grams. The values of K_d increase with the increasing of temperature (Table 6), indicating the endothermic process.

The standard enthalpy change ΔH^0 (J/mol) and entropy change ΔS^0 (J/mol/K) of the adsorption were estimated by plotting ΔG^0 versus T in eqn. (13).

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \qquad\qquad (13)$$

The slope and the intercept (Figure 8), give the values of ΔH^0 and ΔS^0 respectively (Table 6). From Table 6 the $\Delta G^0 < 0$ (negative values) at 20, 40 and 60°C. This value indicates that Ni(II) sorption process is spontaneous and the $\Delta S^0 > 0$ (positive values) indicate the increase in the randomness in the interface of solid phase / solution phase through the sorption process [40,41], reflect the affinity of the PSAHB-SO$_3$H adsorbent for Ni^{2+} ions, and finally suggest some structural changes in the nickel-sorbent [42]. The $\Delta H^0 > 0$ confirm that sorption process is endothermic [41].
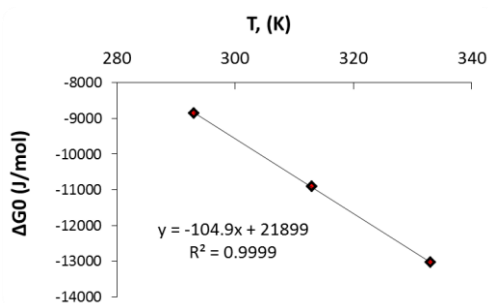

Figure 8. Gibbs free energy changes vs. Temperature in the adsorption of Ni(II) on PSAHB-SO$_3$H sorbent

Table 6. Thermodynamic parameters for the adsorption of Ni^{2+} onto PSAHB-SO$_3$H, t=20 min

T(K)	K$_d$	G^0 J/mol	ΔH^0 J/mol	ΔS^0 J/mol. K	R^2
293	37.78	-8846.88	21899	104.9	0.999
313	66.33	-10915.8			
333	111.17	-13042.9			

Acidic Properties of The complex Adsorbent

The determination of acidic dissociation constants (pK$_{ion}$) is an essential step in the examination of the physic-chemical properties of chelating polymer adsorbents. The pK$_{ion}$ of adsorbents determine their reactivity and the stability of formed complexes [43].

Figure 9 of $\dfrac{\Delta pH}{\Delta Q}$ - Q differential curve for PSAHB-SO$_3$H adsorbent shows the positions of the equivalence points that correspond to the contents of individual types of chelating groups SSC$_{indi}$ in the adsorbent phase (Figure 9). It is clear that the PSAHB-SO$_3$H adsorbent contains three different ionogenic groups : N=N-group, SO$_3$H and -OH group.
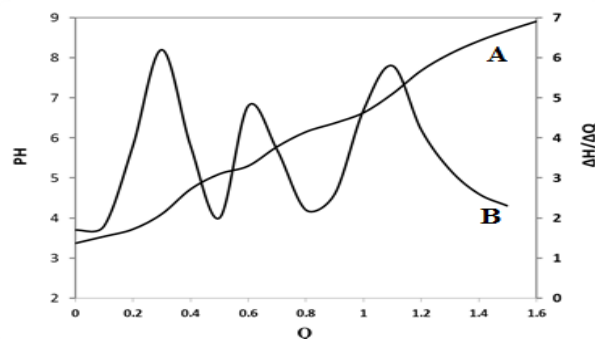
Figure 9. (A) Integral and (B) differential curves of potentiometric titration of PSAHB-SO₃H adsorbent

According to the modified Henderson-Hasselbalch in (eqn. (5)), the pH of the solution should be a linear function of $\log\frac{\alpha}{1-\alpha}$ with a slope of m ~1. The slope of the linear dependence used to calculate the pK$_{ion}$ values for the chelating groups of the adsorbent (Figure 10). The graphical determination of the pK$_{ion}$ values showed that first ionization stage of -N=N-group, pK$_1$=4.27, second ionization stage of SO₃H, pK$_2$=6.36, and the third ionization stage of -OH group, pK$_3$=7.95 (Figure 10). The pK$_{ion}$ values of the adsorbent under study were determined experimentally and graphically and presented in Table 7.
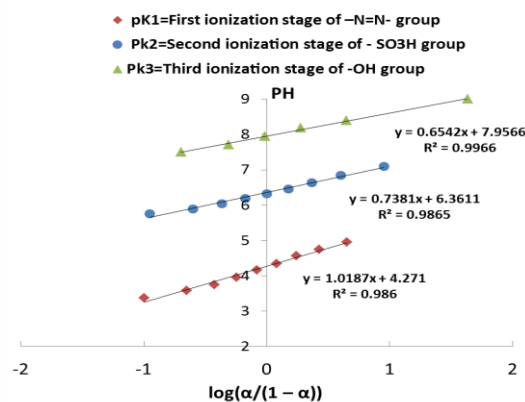

Figure 10. Determination of ionization constants for the adsorbent by the graphical method.

Table 7. Ionization constants of PSAHB-SO₃H adsorbent

First ionization stage	pK (Graphical method)	pK (Calculation) *		
		$\bar{x}$	Sr	$\bar{x} \pm \delta$
First ionization stage	5.03 (m=1.02)	5.01	0.01	5.01 ± 0.05
Second ionization stage	6.36 (m=0.74)	7.15	0.007	7.15 ± 0.03
Third ionization stage	7.97 (m=0.65)	8.63	0.006	8.63 ± 0.04

Note: * The results expressed as $\bar{x} \pm st/n^{1/2}$ where is the $\bar{x}$ mean of n observations of $\bar{x}$, s is the standard deviation, t is distribution value chosen for 95% confidence level. S$_r$ is the relative standard deviation [29].

Adsorption Mechanism

FT-IR analysis: The IR spectrum of the PSAHB-SO₃H adsorbent and its complex with Ni(II) is shown in Figure 11. To suggest a processes for the adsorption of Ni^{+2} ions on PSAHB-SO₃H adsorbent, FT-IR analysis was carried

out (Figure 11) of the adsorbent before (a) and after (b) the adsorption process. In this study a processes is proposed based on ion exchange by the following active chlating groups: negativelly charged of dphenol oxygen atom with positively charged of Ni^{+2} ions. This groups are capable of bonding Ni^{+2} ions during the dissociation of a H^+ [13]. Based on the FT-IR spectra obtained, it can be deduced that after the adsorption of Ni^{+2} ions onto PSAHB-SO$_3$H adsorbent, the intensity of the relevant bands is reduced. This is visible in the stretching vibrations of -OH groups in the range 3560-3350 cm^{-1}and the vibrations of -N=N-groups in the 1630 cm^{-1}. The obtained sigles in IR spectra show visibly that Ni^{+2} ions form bonds with oxygen groups, at the same time causing separation of a H^+ cation. Verification of this are slightly shifts in the wavenumbers of the signals fowllowing the interactions of Ni^{+2} ions with active chelating groups on adsorbant surface. For example, maximal wavenumber for the signal -OH groups, is around 3420 cm^{-1}, and after adsorption of nickel ions is shifted to the 3385 cm^{-1}. Similar, the maximal wavenumber for signal N=N groups is around 1630 cm^{-1} befor adsotption and after wes shifted to the 1618 cm^{-1}.
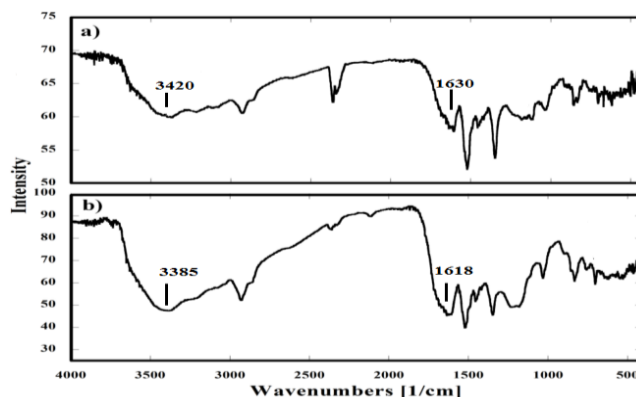

Figure 11. FT-IR spectra before (a) and after (b) the adsorption process for nickel(II) ions

The totality of the data obtained (the known structure of the chelating groups on polymeric matrix, the literature data on the structure of element-chelate adsorbent complex, the number of protons liberated during adsorption (n), and FT-IR analysis) allowed us to suggest the most probable structure of the nickel-PSAHB-SO$_3$H complex as in (Figure 12). In this complex structure, a nickel ion bound by a covalent bond to a phenol oxygen atom; by one coordinative bond with the azo-group nitrogen atom. The single positive charge of the nickel atom compensated for by the anions of the buffer solution.

Number of Protons Exchange in Adsorption Possesses

The number of liberated protons (*n*) during the adsorption of Ni(II) on PSAHB-SO3H adsorbent determined by the Astakhov method [44,45]. From the pH values and the R% of Ni(II) ions, the number of liberated protons was calculated from the slope of the $\log \dfrac{R}{100-R}$ - *pH* curve (Figure 12); was found one proton to be displaced for a Ni(II) ion in this system, where the slope of the curve=1.055; therefore, the liberated protons *n=1*. The mechanism of nickel sorption in this system defined as follows:

$$H_2R + Ni^{+2} \rightarrow H^+ + NiHR^+$$
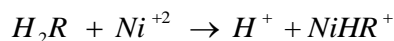
Where H$_2$R refers to the chelating groups in the adsorbent (-OH and -N=N-) and NiHR$^+$ refers to the formed complex.
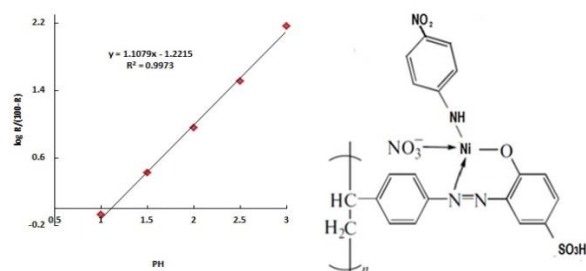
Figure 12. (A) Number of proton (n) substituted in Ni(II) adsorption, (B)Suggested structure of the ternary complex

CONCLUSION

A new polystyrene azo phenol chelating adsorbents well characterized. These adsorbents exhibited high adsorption capacity toward Ni(II) from their aqueous solutions. The adsorption efficiency depends on solution's pH, metal ions concentration, contact time and temperature of adsorption. The optimum adsorption (pH_{opt}) of all adsorbents were in the range of 3-7. Our studies showed that PSAHB-SO$_3$H adsorbent is most promising for preconcentration and separation of nickel(II) from artificial and natural solutions. The obtained results for this adsorbent showed that the Langmuir isotherm model gives better fit to adsorption isotherm results. The kinetic studies exhibited that adsorption can be obeyed to pseudo-second order model. Thermodynamic parameters including ΔG^0, ΔH^0 and ΔS^0 studied. The negative value of ΔG^0 and positive values of ΔH^0 and ΔS^0 clarify that the spontaneous nature of adsorption and endothermic heat of adsorption. The graphical determination of the pK$_{ion}$ values yielded that first ionization stage of -N=N-group (pK$_1$)=4.27, second ionization stage of SO$_3$H group (pK$_2$)=6.36 and the third ionization stage of -OH group (pK$_3$)=7.95. The mechanism of Ni^{2+} removal by PSAHB-SO$_3$H suggest that N^{2+} cation forms a covalent bond with the phenol oxygen atom, a coordination bond with the nitrogen atom of the azo group and the single positive charge of the nickel atom is compensated for by the anions of the buffer solution.

The obtained experimental data can be used in the complex compound chemistry for the development of procedures for preconcentration and separation of trace amounts of Ni^{+2} ions from natural and waste water and naturally-occurring and industrial materials.

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