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Influence of the support base on the sorption of Co(II) with mixed solvents

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Abstract

Theonyltrifluoroacetone (TTA) mixed with trioctyl phosphine oxide (TOPO) have been supported on Amberlite XAD-4, silica gel and wood powder. The resulting resins have been used to study the sorption of cobalt(II) from acetate buffer and their sorption capacities were determined and were found to be 12.38, 11.61 and 6.51 mg g^{-1} for TTA + TOPO/Amberlite XAD4, TTA + TOPO/silica gel and TTA + TOPO/wood, respectively. The experimental results showed that the sorption of Co(II) increases with its initial concentration. The results can be fitted by Freundlich isotherm in the studied cobalt concentration range [10^{-4}–10^{-3} M] and $1/n$ values are 1.07, 1.17 and 1.73 for Amberlite XAD4, silica gel and wood powder, respectively. The sorption of Co(II) onto the prepared resins was found to follow the pseudo-second order model and the sorption rate have the values 8.79×10^{-3}, 10×10^{-3} and 16×10^{-3} g mg^{-1} min^{-1} for Amberlite XAD4, silica gel and wood powder, respectively. Thermodynamic parameters have also been calculated for the three systems and sorption process was found to be spontaneous and endothermic one.
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Keywords: Sorption; Co(II); TTA; TOPO; Amberlite XAD-4; Silica gel; Wood

1. Introduction

The removal of intermediate and low radionuclides from radioactive aqueous waste is a matter of great interest in the field of waste management. Cobalt (^{58}Co and ^{60}Co), cesium (^{134}Cs and ^{137}Cs) and strontium (^{85}Sr and ^{90}Sr) are considered from the most serious nuclides in this waste due to their relatively long half lives and their quantities. In addition, ^{60}Co is characterized by emission of high gamma energy (1.17 and 1.34 Mev) which is employed widely in medicine and nuclear industries. So, the separation of cobalt from the radio waste is an important step. Different techniques such as precipitation, oxidation/reduction [1], ion exchange [2], solvent extraction [3] and sorption [4] have been applied to recover the metal ions from aqueous solutions but in the recent years, the solid–liquid technique has come at the forefront. This is due to the superior characteristics of this technique since it is considered as a link between solvent extraction and ion exchange and characterized by its high binding capacity, selectivity towards different elements and enhancement of the mobility of extractant in the resin surface. Valuable researches on the sorption and separation of metal ions with solid-liquid or solvent impregnated resin technique have been carried out [5–7].

The most common extractants used are organophosphorous compounds as tri-butyl phosphate (TBP) [8], di (2-ethyl hexyl) phosphoric acid (DEHPA) [9–12], bifunction carbamoylmethyl phosphine oxide [13] and organophosphonate [14]. Also, some extractants as tri-octyl amine [15], quaternary ammonium salts [16] and hydroxy quinoline [17] have rarely been used. Silica gel, Amberlite XAD series and cellulose powder have been used as supporting materials in such techniques. Until now, only a few studies have shown that the impregnated resin with mixed solvents exhibit good efficiency for the separation of metal ions [18].

Sekine and Dyrssen [19] and Ramadan [20] have used a mixture of TTA and TOPO to study the extraction of some divalent ions as Sr(II), Ca(II) and Co(II) from aqueous solutions. They found that the logarithmic values of equilibrium constant for the complexes $Sr(TTA)_2$.TOPO, $Ca(TTA)_2$TOPO and $Co(TTA)_2$TOPO are −9.91, −6.76 and −3.68, respectively. So, it could be observed that Co-complex has the highest stability with respect to the other complexes.

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Thus in this work, TTA and TOPO mixture supported on different bases viz—Amberlite XAD4, silica gel and wood powder in a trial to prepare impregnated resin with mixed solvents and using them to study the sorption of $^{60}Co^{2+}$ from aqueous solution. Different parameters were studied to optimize the sorption process. The effect of the presence of some interfering ions like Cs^{+} and Sr^{2+} on Co^{2+} separation was studied.

2. Experimental

2.1. Reagents

TTA and TOPO were supported from Merck and Eastman Organic Chemicals and used as extractants. Amberlite XAD4 resin with mesh number (20–60), surface area 725 m^2/g, porosity% 45, true weight density 1.02 and average pore diameter 4–9 nm. Silica gel is an analytical grade with mesh number (70–230) and having pore diameter 60 Å. Both resins were obtained from Fluka while wood powder was obtained from Inshas region. Wood was grinded and sieved to give the particle diameter 0.1–0.4 mm.

2.2. Purification of bases

The three bases were washed several times with acetone and water to eliminate any foreign materials. The materials were filtrated, dried at 40 °C for 48 h and kept in a desecator for further usage.

2.3. Preparation of impregnated resins

The dry method is applied for the preparation of mixed solvent impregnated resins. In this method, a fixed weights 2.77 and 0.20 g of TTA and TOPO, respectively were dissolved in 125 ml benzene then 40 ml of the solvents in benzene were mixed with 3 g of either support base Amberlite XAD4, silica gel or wood powder until all organic solution was absorbed. Then the impregnated resins were dried at 40 ± 2 °C for 48 h.

In order to detect the fixation of solvents into the supported base, an amount of 0.1 g of either impregnated resin TTA + TOPO/Amberlite XAD4 or TTA + TOPO/silica gel or TTA + TOPO/wood was shaken with 10 ml of acetate buffer for 48 h. Then TTA was determined spectrophotometrically in aqueous solution at wave length 325 nm. The librated percentage of TTA and TOPO into aqueous solution did not exceed 5%. The surface area of untreated silica gel and wood powder was measured using BET technique and found to be 422 and 7.1 m^2/g for silica gel and wood, respectively and these values were decreased to 322.49 and 6.91 m^2/g after impregnation with TTA + TOPO and this decrease was also observed for surface area of TTA + TOPO/Amberlite XAD4 and found to be 466.73 m^2/g. This behavior could be attributed to the coating of pores of support bases by organic solvents which decrease the penetration of N_2 into some pores. The measurements of surface area and pore diameter were performed using pore size micrometer-9320, USA.

2.4. Preparation of $^{60}Co^{2+}$

The radioactive cobalt is prepared by irradiation of cobalt oxide for two days in Egyptian Et-RR-1 nuclear reactor.

2.5. Procedure

The sorption of cobalt(II) was studied by batch equilibration experiments. 0.05 g of either prepared resins was shaken well with 5 ml of acetate buffer spiked with radioactive cobalt in thermo-stated shaker of the type SW-20C/2 from Julobo laboratories GmbH, Germany. After equilibration and centrifugation, 1 ml of aqueous solution was withdrawn for gamma-ray estimation using Nucleus 500 connected to NaI crystal. The distribution coefficient (K_d) and uptake % (U%) of cobalt were calculated from following equations.

$$K_d = \frac{A_o - A}{A} \times \frac{V}{m}\,(\text{ml/g}) \quad (1)$$

$$U\% = \frac{A_o - A}{A_o} \times 100\,(\%) \quad (2)$$

where, A_o and A are the activities expressed in counts per minute of 1 ml solution for the radioisotope before and after contacting the resin, V is the volume of the aqueous phase in milliliter and m is the weight of dry resin in gram.

3. Results and discussion

3.1. I.R. spectra

I.R. spectra of free support bases and impregnated resins are given in Fig. 1a–c. Fig. 1a represents I.R. spectra for untreated Amberlite XAD4 and TTA + TOPO/Amberlite XAD4. The spectra for free Amberlite XAD4 show characteristic peak at 3458 cm^{-1} that is related to O–H stretching vibration of H_2O molecules. The absorption bands at 2851–3015 cm^{-1} are ascribed to aromatic and aliphatic C–H stretching and the peaks at 1444–1640 cm^{-1} for C=C ring stretching. The spectra for TTA + TOPO/Amberlite XAD4 shows the shift and decrease in the intensity of stretching C–H and C=C bands at 2928 and 1444–1640 cm^{-1}, respectively. This change may be referred to the role of π-electrons of C=C in immobilization of TTA and TOPO on Amberlite XAD4. Also, the appearance of new peaks at 1702, 1110.3–1290.64 cm^{-1} which are characteristic for keto C=O, phosphoryl group P=O and P–O–C stretching vibration confirms the incorporation of solvents into Amberlite XAD4. Fig. 1b represents I.R. spectra for TTA + TOPO/silica gel. There are intense peaks at 1656.36 and 1079 cm^{-1} which are characterized for keto and phosphoryl groups, respectively. Peaks at 955, 790 and 723 cm^{-1} which are assigned for C–H and C=C out of plane (flexion). In addition to sharp absorption peak at 481 cm^{-1} which indicates the presence of oxygenated inorganic constituents, I.R. spectra of wood and TTA + TOPO/wood are represented in Fig. 1c. The spectra of untreated wood show peak at 3433.38 cm^{-1} which is related to O–H stretching from water or hydroxyl groups of cellulose. Also, peak at 2918 cm^{-1} is

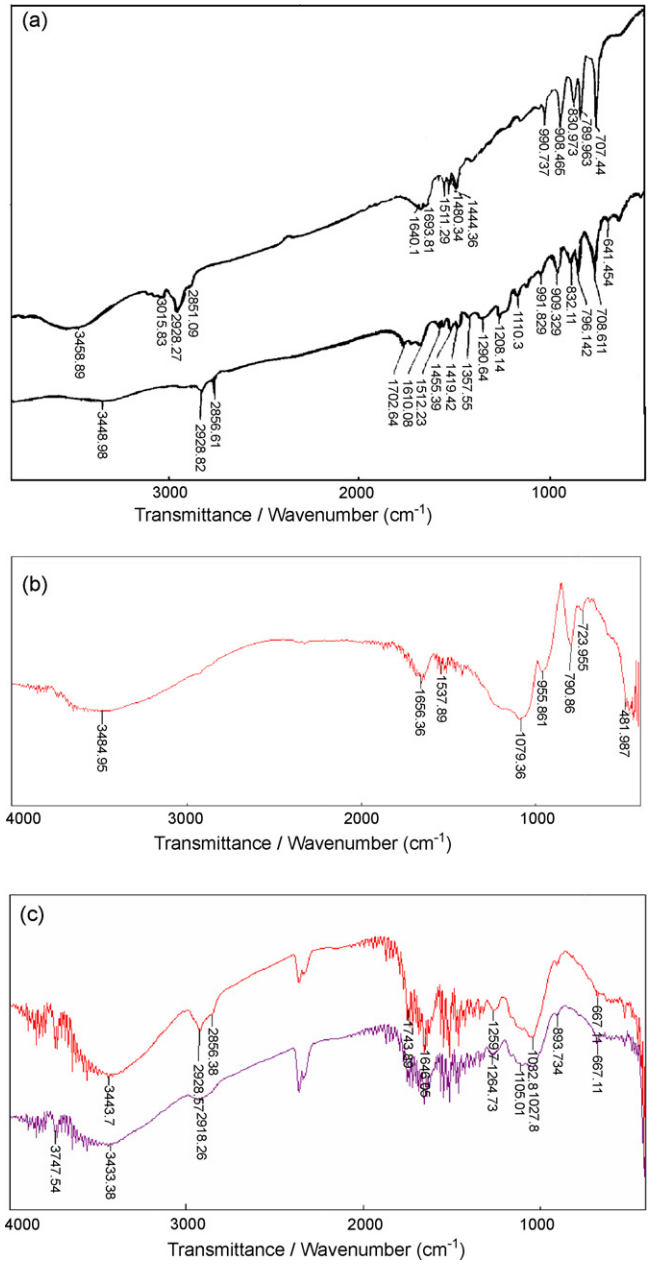
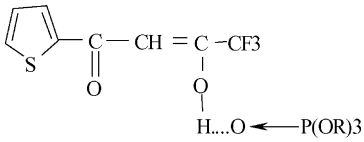


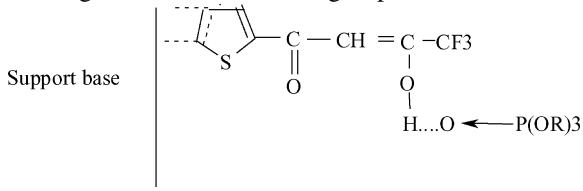
Fig. 1. (a) I.R. spectra; upper for Amberlite XAD4, lower part for impregnated resin TTA + TOPO/Amberlite XAD4; (b) I.R. spectra for impregnated resin TTA + TOPO/silica gel; and (c) I.R. spectra; upper part for wood, lower part for impregnated resin TTA+TOPO/wood.

assigned to the asymmetric stretching band of methyl group. The absorption peaks at 1000–1300 cm^{-1} are characteristic for C–C and C–O stretching and O–H bending. The spectra of impregnated wood show the increase of these peaks intensity, and this increase can be referred to the addition of the stretching peak of phosphoryl group. The appearance of new absorption band at 1742 cm^{-1} is assigned for keto group which confirms that TTA and TOPO are impregnated on wood powder.

The literature mentioned that HTTA and many other B-diketones may exist in keto, enol and keto hydrate form and the medium affects greatly on keto–enol equilibrium. In benzene, TTA is about 90% in enolate form [21] and this form combined with TOPO through the hydrogen bond to give the following structure.



The combined solvents could be impregnated into the support bases through π-electrons of C=C group.



3.2. Adsorption performance

Some preliminary experiments on the sorption of Co(II) onto free bases (Amberlite XAD4 or silica gel or wood powder) were carried out individually and the obtained data show that cobalt is not sorbed completely on free Amberlite XAD4 or silica gel while wood powder records a small sorption percentage of Co(II) which is taken in consideration during calculations related to wood resin. Various parameters affecting the sorption of cobalt as pH, ionic strength, metal ion concentration, temperature were studied to optimize the sorption of cobalt. Also, the effect of the presence of some competing ions in aqueous solution on the sorption of Co(II) was studied.

3.2.1. Effect of pH

The uptake of cobalt from acetate buffer of variable pH values (4.5–6) was studied by the three impregnated resins TTA + TOPO/Amberlite XAD4, TTA + TOPO/silica gel and TTA + TOPO/wood and the obtained results are represented in Fig. 2. From this figure, it is obvious that the uptake percentage of cobalt is slightly increased in pH range 4.35–6. So, it can be said that the acetate buffer of pH 5.6 is suitable for the sorption of divalent cobalt into three prepared resins. This finding agrees with Ramadan [20] who studied the extraction of Co(II) by HTTA and TOPO using liquid–liquid technique and found that the suitable pH is 5.1 and suggested the extraction mechanism as follows:

$$\mathrm{Co(II)} + 2\mathrm{HTTA} + \mathrm{TOPO} \leftrightarrow \mathrm{Co(TTA)_2 \cdot TOPO} + 2\mathrm{H^+} \quad (3)$$

3.2.2. Effect of contact time

The sorption of Co(II) from acetate buffer of pH 5.6 into three prepared impregnated resins is displayed in Fig. 3 as a function of time. The data show that the uptake percentage of Co(II) increases with elapsed time till reached to a fixed value after 3 h. The curves in the figure clarify that the maximum uptake of Co(II) on prepared resins HTTA + TOPO/Amberlite XAD4, HTTA + TOPO/silica gel and HTTA + TOPO/wood is 95, 85 and 57%, respectively. The high sorbability of Amberlite XAD4 and silica gel resins could be referred to their high

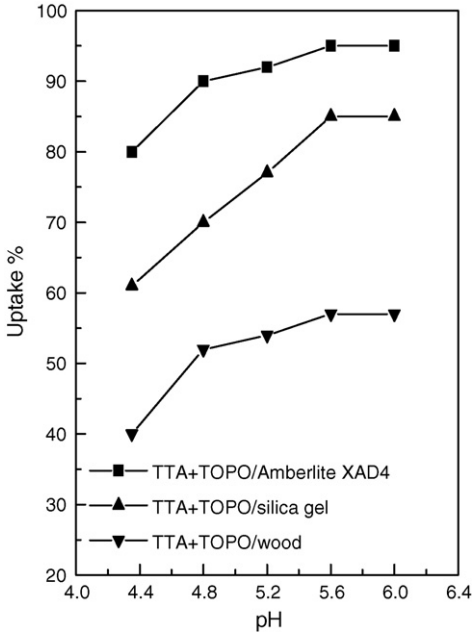


Fig. 2. The effect of pH on the sorption of Co(II) from acetate buffer by TTA + TOPO/base (conditions: $V/m = 100$ (ml/g), $T = 30 \pm 1\,^{\circ}C$ and $[Co] = 4 \times 10^{-6}$ M).

surface area. Ramadan in his study found that the distribution ratio of Co(II) reached nearly 20 which is translated to extraction percent nearly 95% and this value is the same for the sorption of cobalt into Amberlite resin. But the comparison between two techniques clarifies that solid–liquid technique is better from the economical point of view, in addition, it can easily concentrate Co(II) from aqueous solution and hence the regeneration of Co(II) from loaded resin could be achieved.

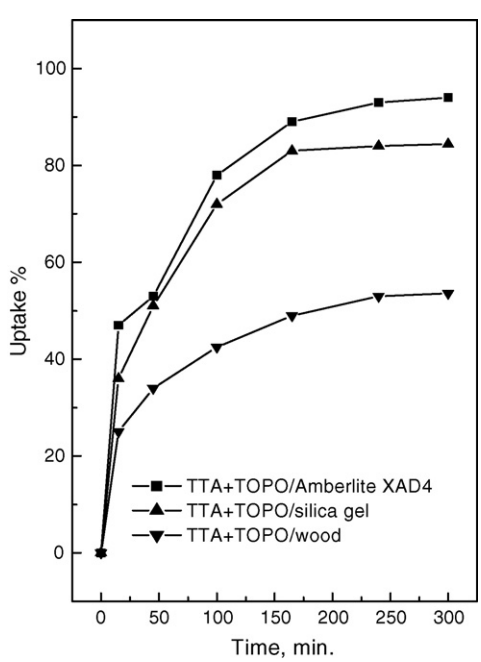


Fig. 3. Sorption of Co(II) by TTA + TOPO/base (Conditions: acetate buffer of pH = 5.6, $V/m = 100$ (ml/g), $T = 30 \pm 1\,^{\circ}C$ and $[Co] = 0.5 \times 10^{-3}$ M).

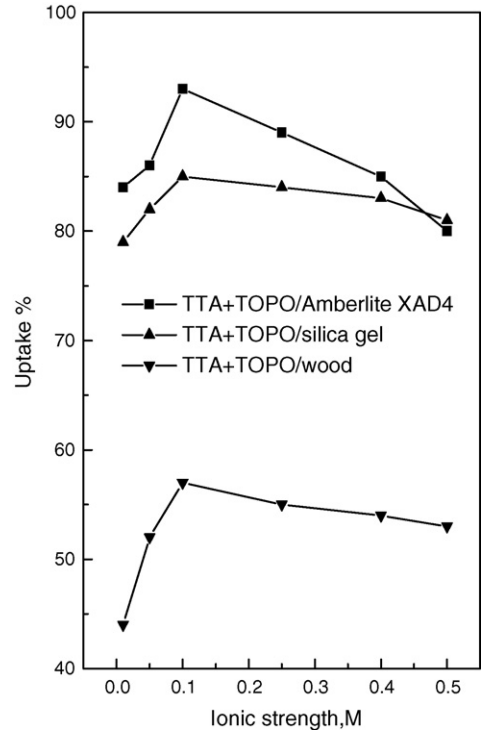


Fig. 4. The effect of ionic strength on the sorption of Co(II) by TTA + TOPO/base (conditions: $V/m = 100$ (ml/g), pH = 5.6, $T = 30 \pm 1\,^{\circ}C$ and $[Co] = 0.5 \times 10^{-3}$ M).

3.2.3. Effect of ionic strength

Different concentrations of sodium acetate were bufferized with acetic acid to obtain aqueous solutions having pH = 5.6 and various ionic strengths. These solutions were spiked with radioactive cobalt and its sorption on the three prepared resins were studied Fig. 4. Data in the figure show that the sorption of Co(II) into three resins has the same behavior. Since the uptake of Co(II) is slightly increased by increasing the ionic strength from 0.01–0.1 M. As the ionic strength is increased after this range, the uptake of Co(II) is obviously decreased with respect to all prepared resins. The enhancement effect of ionic strength in the range (0.01–0.1) may be related to the change in diffusion layer in the presence of strong electrolyte as $NaNO_3$ increases the charge density in the diffusion layer which minimize the volume of diffusion layer required to neutralize the positive charge of cobalt ion. That means sodium nitrate in this range of concentration has thinning effect on the diffusion layer. While the decrease in the removal of cobalt which was observed with aqueous solutions of ionic strength more than 0.1 M may be related to the competition of Na^+ with Co^{2+} on the replaceable active sites of the prepared resins. This decrease was also recorded by Bangash et al. [22] on studying the removal of cobalt on soil and Cheong and Lee [23] for the removal of Co(II) by ferrite process from aqueous solution.

3.2.4. Effect of competing ions

It is well known that cobalt, cesium and strontium are considered from the serious radio nuclides in liquid waste due to their long half-life. In this experiment, 0.5×10^{-3} M $Co^{2+}$is

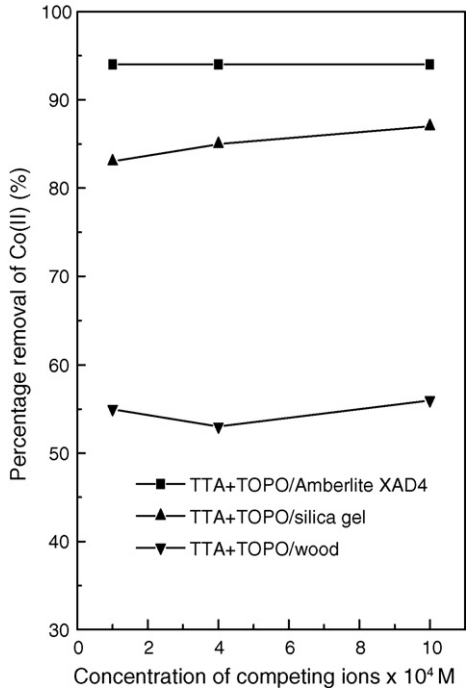


Fig. 5. Competitive phenomenon of Cs^+ against Co^{2+} removal efficiency from acetate buffer of pH 5.6 by TTA + TOPO/base in presence of different concentrations of Cs^+.

mixed with different concentrations of either Cs^+ or Sr^{2+} in the range (10^{-4}–10^{-3} M). The effect of these elements on the uptake of Co(II) on three prepared resins is represented in Figs. 5 and 6. The shown results in the two figures clarify that the maximum uptake of cobalt records the values 95, 85 and 57% on TTA + TOPO/Amberlite XAD4, TTA + TOPO/silica gel and TTA + TOPO/wood, respectively. That means the presence of cesium and strontium in this range of concentration does not affect on the sorption of cobalt. Cheong and Lee [23] recorded this behavior on studying the effect of competing cation, Ca^{2+} on the removal of cobalt by ferrite method. This behavior could be referred to large ionic radii of Sr^{2+} and Cs^+ compared with Co^{2+} since ionic radii of Sr^{2+}, Cs^+ and Co^{2+} are 1.13, 1.69 and 0.76 A, respectively. This relative small ionic radius of Co(II) facilitate its interaction with TTA^- and, consequently, its penetration in impregnated resin.

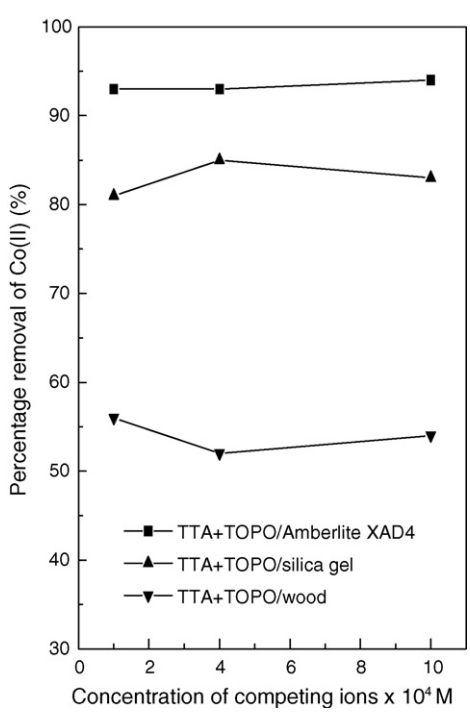


Fig. 6. Competitive phenomenon of Sr^{2+} against Co^{2+} removal efficiency from acetate buffer of pH 5.6 by TTA + TOPO/base in presence of different concentrations of Sr^{2+}.

3.3. Reproducibility

The reproducibility of the sorption data within batch experiments was clarified by measuring the sorption of Co(II) onto TTA + TOPO/Amberlite XAD4, TTA + TOPO/silica gel and TTA + TOPO/wood. The experiments were performed four times. The standard deviation for the distribution coefficients ΔK_d was calculated from the following equation

$$\Delta K_d = \sqrt{\frac{\Sigma(K_d^- - K_d)^2}{n-1}} \quad (4)$$

where K_d is distribution coefficient for an experiment, K_d^- is the mean value of distribution coefficient of all experiments and n is the number of experiments carried out under the same experimental conditions. The calculated values for K_d, K_d^- and ΔK_d are tabulated in Table 1. From these values, it can be observed that the standard deviations do not exceed 2.7%.

3.4. Sorption capacity

The sorption capacity of the three prepared resins was estimated through batch technique by equilibrating 0.1 g of either resin with 10 ml of Co(II) solution under the optimum conditions which are mentioned above. The uptake percentage of Co(II) was calculated and cobalt solution withdrawn and replaced by another new one and this process is repeated till the uptake % reached zero and the sorption capacity was calculated from the relation:

$$\text{Capacity in (mg g}^{-1}) = \frac{\%U}{100} \times C_o \times Z \times \frac{V}{m} \quad (5)$$

Table 1
standard deviation for distribution coefficients of Co(II) into AmberliteXAD4, sillica gel and wood resins

Resin/K_d	Co-Amberlite resin	Co-silica gel resin	Co-wood resin
1st experiment	1896	585	132
2nd experiment	1894.5	583.6	131.3
3rd experiment	1901	582	133.7
4th experiment	1897.2	587.1	135
Mean value (k_d^-)	1896.6	584.4	133
Standard deviation(ΔK_d)	2.68	2.16	1.67

where, $\%U$ is the percentage uptake (% removal), C_o is the initial concentration of element (g/ml), m is the weight of adsorbent (g), V is volume of the aqueous phase (ml) and Z is the charge of metal ion. The sorption capacity of TTA + TOPO/Amberlite XAD4, TTA + TOPO/silica gel and TTA + TOPO/wood for Co(II) were found to be 12.38, 11.61 and 6.51 mg g^{-1}, respectively. These values are in accordance with the specific surface area sequence of prepared materials since their values are 466.76, 322.49 and 6.91 m^2/g.

Muraviev [24] in 1998 mentioned that the capacity of solvent impregnated resins depends on the concentration of extractant in the impregnating (organic) solution, the swelling of the polymer beads in this solution and the porosity of the polymer. In this study, the first parameter is excluded as the concentration of combined solvents is fixed with respect to the three bases, the other parameters are effective in the preparation of the three resins. In this concern, many researches have mentioned that Amberlite XAD4 [24] and silica gel [25] have high swelling in the organic solvents while the swelling of wood is slight due to the hydrogen bonding properties of organic liquids [26]. The porosity of the polymer is another parameter which strongly influences the capacity of the resins [27] since the high porosity of the polymeric support leads to higher volumetric uptake of the organic solvents. The porosity of Amberlite XAD4 is 45% with average pore diameter 4–9 nm Also, Renat in1992 [28] said that silica gel with surface area 175–800 m^2 g^{-1} is characterized by high porosity when being dried while the wood powder has low porosity with avg. pore volume 0.7 nm. In addition, the extent of sorption is directly proportional to specific surface area of the solid sorbent. This may be based on the increase in sorbent surface area which results in an increase in the planner distributed pores, therefore the element will highly penetrate into the sorbent surface achieving a high extent of sorption [29].

3.5. Adsorption kinetics

3.5.1. Effect of cobalt concentrations

The three prepared resins are used to study the sorption of Co(II) from aqueous solutions of acetate buffer (pH = 5.6 and I_o = 0.1 M) having different concentrations of Co(II) (10^{-4}–10^{-3} M) to clarify the influence of initial cobalt concentrations on its removal by the resins Figs. 7–9. The data show that the extent of sorption increases with increasing the initial concentration of cobalt and this behavior means that the external mass transfer may be the prevalent sorption mechanism

3.5.2. Adsorption rate

The represented data in Figs. 7–9 clarify that the removal of cobalt by prepared resins takes place through two steps; the first one involves the rapid removal within 40 min followed by slower one in the next 140 min and to investigate the sorption rate law of cobalt, the two kinetic models (Lagergren [30] and Ho et al. [31–33]) were applied for an initial cobalt concentration 5×10^{-4} M.

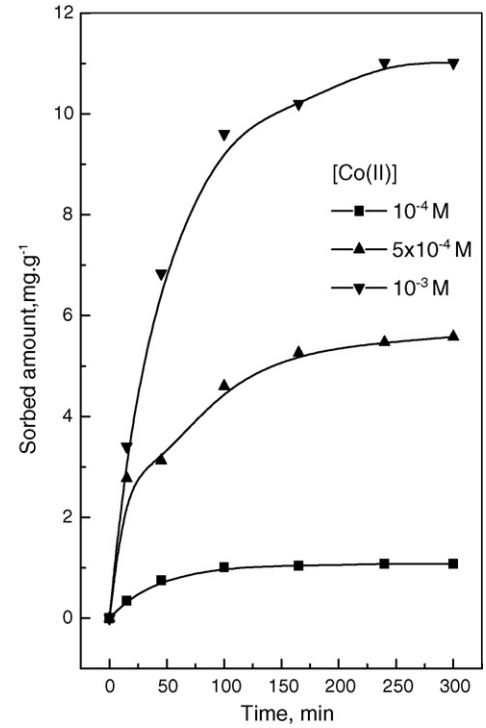


Fig. 7. The effect of Co(II) initial concs. on its sorption by TTA + TOPO/AmberliteXAD4 (conditions: V/m = 100 (ml/g), pH = 5.6, I_o = 0.1 M and T = 30 ± 1 °C).

Lagergren equation

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{kt}{2.303} \quad (6)$$

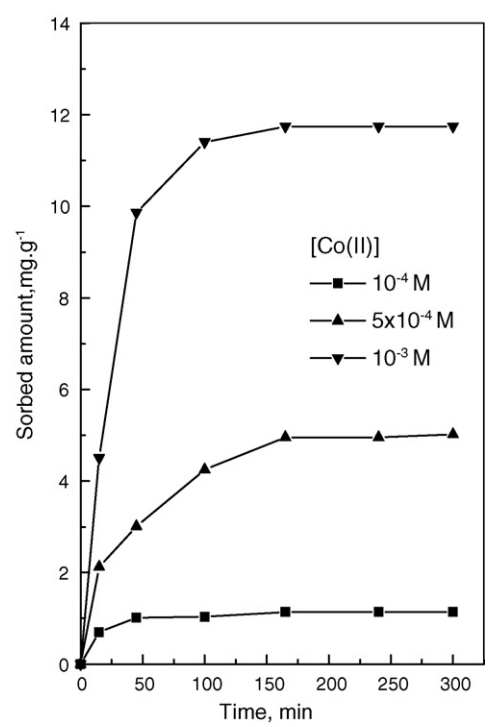


Fig. 8. The effect of Co(II) initial concs. on its sorption by TTA + TOPO/silica gel (conditions: V/m = 100 (ml/g), pH = 5.6, I_o = 0.1 M and T = 30 ± 1 °C).

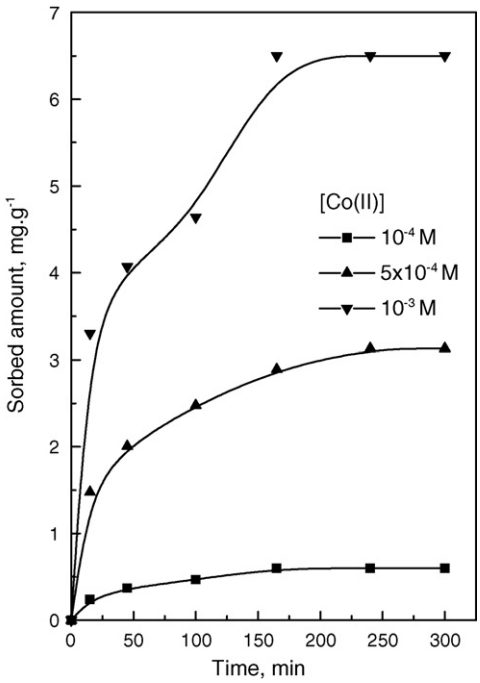


Fig. 9. The effect of Co(II) initial on its sorption by TTA + TOPO/wood (conditions: $V/m = 100$ (ml/g), pH = 5.6, $I_o = 0.1$ M and $T = 30 \pm 1$ °C).

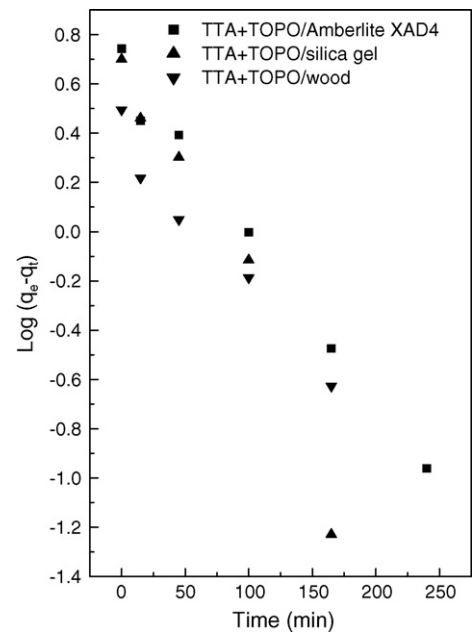


Fig. 10. The pseudo-first order model for the sorption of Co into TTA + TOPO/resins. (conditions: $C_o = 0.5 \times 10^{-3}$ M, $V/m = 100$ (ml/g), pH = 5.6 and $T = 30 \pm 1$ °C).

Ho equation

The pseudo second order equation proposed by Ho et al. in its differential form is

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{7}$$

by integrating the equation for initial conditions $t = o$ and $q_o = 0$ given

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + kt \tag{8}$$

and Eq. (7) can be arranged to give the linear form

$$\frac{t}{q_t} = \left(\frac{1}{kq_{eq}^2}\right) + \left(\frac{t}{(q_{eq})}\right) \tag{9}$$

where q_t and q_{eq} are the amounts of Co(II) adsorbed at time t(min) and equilibrium time, respectively and k is the rate constant of adsorption process. Figs. 10 and 11 represent the application of Lagergren and Ho models, respectively. By comparing the data in two figures it can be observed that data in Fig. 10 is more scatter than data in Fig. 11. So, it can be concluded that the experimental data for sorption of Co(II) on prepared materials follows the pseudo-second order model that means the rate determine step involving the exchange of electrons between cobalt and mixed solvents (TTA + TOPO). This behavior agrees with others who studied the sorption of divalent elements using the solid–liquid technique [34–36]. From the plots in Fig. 11, the equilibrium amount and sorption rate of cobalt on prepared resins are calculated and tabulated in Table 2.

By comparing the tabulated data, it can be observed that Amberlite resin has the highest equilibrium amount of cobalt followed by silica resin while wood resin exhibits the highest sorption rate with respect to the two other resins.

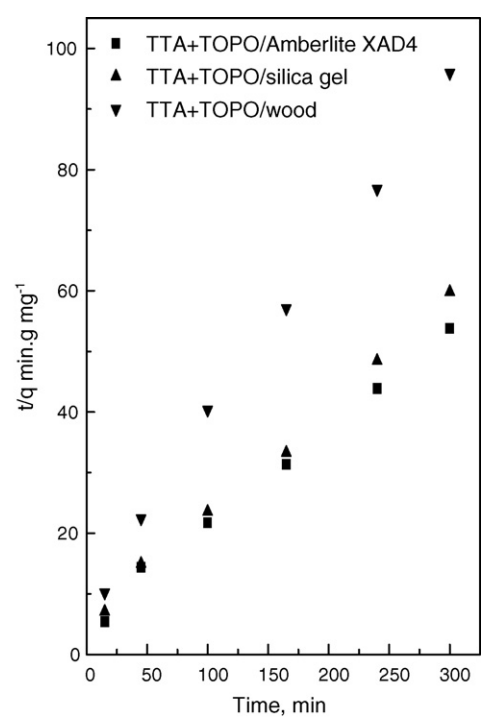


Fig. 11. Pseudo-second order model for sorption of Co(II) into TTA + TOPO resins(conditions: $C_o = 0.5 \times 10^{-3}$ M, $V/m = 100$ (ml/g), pH = 5.6 and $T = 30 \pm 1$ °C).

Table 2
Kinetic parameters of Ho et al. model for sorption of Co(II) into TTA + TOPO resins

Sorbents	q_{eq} (mg g^{-1})	k (g mg^{-1} min^{-1})	Correlation coefficient (r^2)
TTA + TOPO/Amberlite XAD4	5.86	8.79×10^{-3}	0.994
TTA + TOPO/silica gel	5.31	10×10^{-3}	0.995
TTA + TOPO/wood	3.29	16×10^{-3}	0.995

3.6. Sorption isotherm

The cobalt concentration dependence study on the three prepared resins were also subjected to analysis in terms of Langmuir and Freundlich isotherms which are suitable for describing the sorption of mono component (metal ions) by different materials [37,38]. Langmuir model has the following assumptions—adsorption occurs on fixed number of active sites and each one can hold only one molecule. Thus, only monolayer coverage is permitted – adsorption is reversible – adsorption energy is constant for all sites and there is no lateral interaction between the adsorbate molecules and this model can be represented by the following equation:

$$\frac{1}{q_e} = \left(\frac{1}{Q}\right) + \left(\frac{1}{bQ} \times \frac{1}{C_e}\right) \quad (10)$$

where C_e is the equilibrium concentration (mg L^{-1}), Q is monolayer sorption capacity and b is a constant related to energy of adsorption. The relation between $1/q_e$ and $1/C_e$ is represented in Fig. 12. The data in the figures shows a group of straight lines with intercepts 0.0157, 0.0462 and 0.569 for the relation of Co(II) sorption by HTTA + TOPO/Amberlite XAD4, HTTA + TOPO/silica gel and HTTA + TOPO/wood, respectively, that means that the corresponding monolayer sorption capacities have the values 63.70, 21.64 and 1.76 mg g^{-1} for Amberlite XAD-4, silica gel and wood resins, respectively. But these values are very far from the values obtained by the experimental data. So it can be said that the data do not fit the Langmuir equation. However, the Freundlich adsorption isotherm was capable of describing the obtained data. Freundlich model is another widely used adsorption isotherm represents the relation between solute concentration and adsorbent surface affinity. Freundlich equation is represented by the following formula:

$$\log q = (\log K) + \left(\frac{1}{n}\right)(\log C_e) \quad (11)$$

where K and $1/n$ are Freundlich constants.

The relation between $\log q$ and $\log C_e$ is represented in Fig. 13. The correlation coefficient for the linear regression of sorption Co(II) by three resins records the values 0.999, 0.997 and 0.954 for Amberlite XAD4, silica gel and wood resins, respectively and their corresponding $1/n$ values are 1.06, 1.17 and 1.74 indicating that favored adsorption process occurred on the surface of adsorbent.

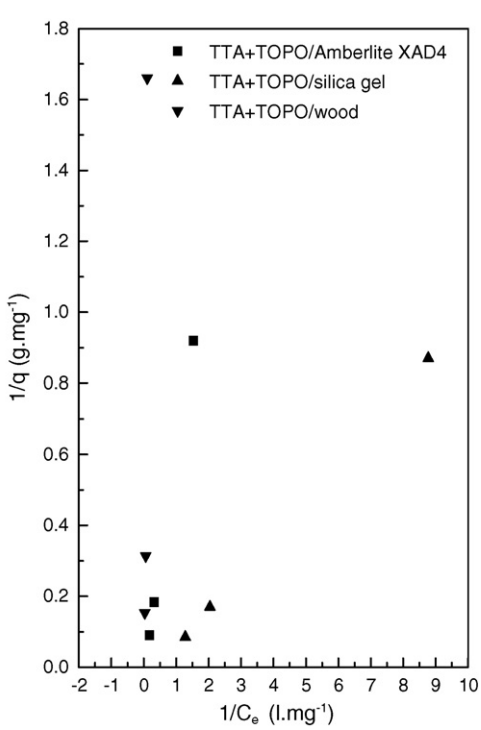


Fig. 12. Langmuir relation for the sorption of Co(II) by TTA + TOPO/base (conditions: acetate buffer of pH = 5.6, V/m = 100 (ml/g), and T = 30 ± 1 °C).

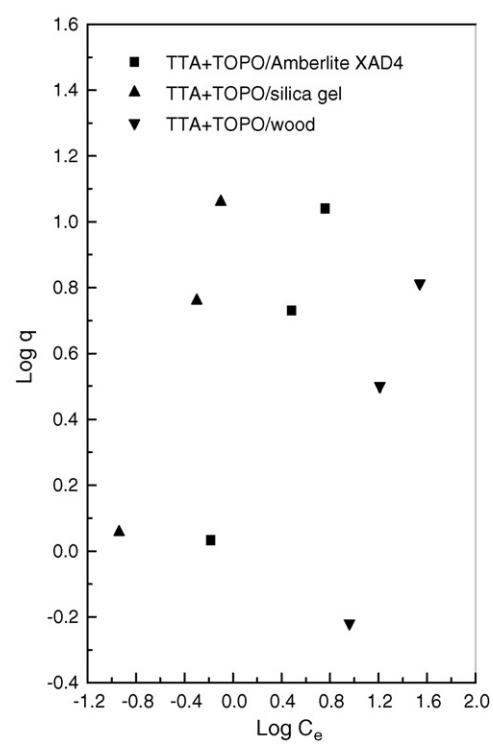


Fig. 13. Frendlich isotherm for the sorption of Co(II) by TTA + TOPO/base (conditions: acetate buffer of pH = 5.6, V/m = 100 (ml/g), T = 30 ± 1 °C).

Table 3
Adsorption studies of Co(II) by TTA + TOPO/base as a function of temperature (V/m = 100 (ml/g), shaking time = 5 h, aqueous solution acetate buffer of pH = 5.6, I_o = 0.1 M and [Co] = 0.5 × 10^{-3} M)

Temp. (°K)	Thermodynamic parameters								
	TTA + TOPO/AmberliteXAD-4			TTA + TOPO/silica gel			TTA + TOPO/wood		
	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS J/(mol k)	ΔH (kJ/mol)	ΔG (kJ/mol)l	ΔS J/(mol k)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS J/(mol k)
303		−18.26	218.61		−16.40	321.17		−11.99	234.68
308	47.98	−19.61	219.44	80.91	−18.16	321.67	59.12	−12.98	234.09
313		−20.51	218.78		−19.72	321.5		−14.45	234.01

3.7. Effect of temperature

The temperature dependence of Co(II) sorption onto prepared resins was studied under the optimized conditions at three different temperatures 303, 308 and 313 K. The calculated distribution coefficients of Co(II) K_d show the increase of their values with an increase in temperature and this proportionality between raising of temperature and distribution of Co(II) may be referred to acceleration of some slow adsorption steps or to creation of some new active sites on the adsorbent surface [39] Plotting the values of log K_d against $1/T$ for the sorption of Co(II) by three resins gives linear relations represented in Fig. 14. From the slopes of these lines, the enthalpy changes (ΔH) were calculated and consequently, the Gibbs free energy (ΔG) and entropy change (ΔS) from the following relations:

$$\log K_d = \left(\frac{\Delta S}{2.303\,T}\right) - \left(\frac{\Delta H}{2.303\,RT}\right) \tag{12}$$

$$\Delta G = -2.303\,RT\ \log\ K_d \tag{13}$$

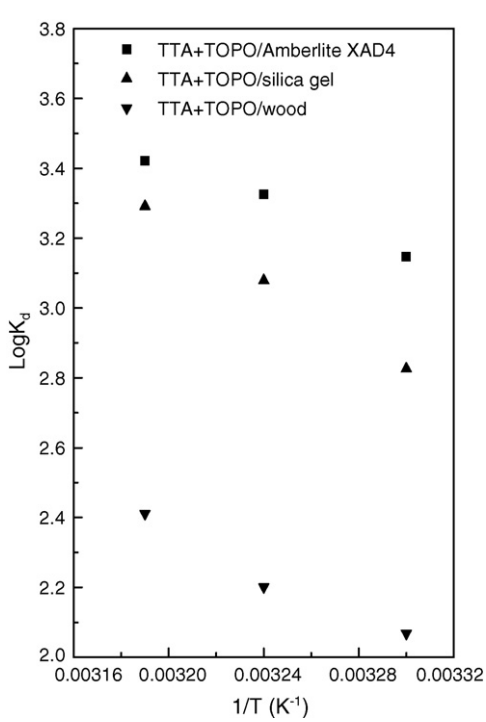


Fig. 14. The relation between log K_d and $1/T$.

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{14}$$

The obtained thermodynamic functions are tabulated in Table 3. The positive values of enthalpy change (ΔH) reflects the endothermic sorption process and this value for Amberlite resin is nearly 47.98 kJ/mol which is very close to general ion exchange or chemisorption (8.37–41.86 kJ/mol) [40], whereas the negative values of (ΔG) indicates that the sorption of Co(II) on three resins is spontaneous one. The positive values of (ΔS) indicate the increased randomness at the solid–liquid interface during the sorption process. This randomness could be attributed to the dehydration of Co(II) during the complex formation in addition to the steric hindrance which caused by TTA and TOPO.

4. Conclusion

Mixed solvents of theonyltriflouroacetone and trioctylphosphine oxide can be fixed successfully into Amberlite XAD4, silica gel and wood. The resultant resins were found to be effective in the sorption of Co(II) from acetate buffer of pH = 5.6. The uptake of Co(II) on these resins reached to 95%, 85% and 57%, respectively within about 1.5–3 h. In spite of low Co(II) uptake on wood resin, wood is considered a cheap by-product of workshops concerning the other resins. The presence of cesium or strontium in aqueous solution does not affect on the removal percent of Co(II) by prepared resins. The sorption of Co(II) was found to follow the pseudo-second order model, that means the exchange of electrons between Co(II) and mixed solvents is sharing in the rate determining step. The sorption isotherm study shows that the data is better represented by Freundlich relation. The thermodynamic functions clarify that the sorption process is spontaneous, endothermic and accompanied by increase in randomness.

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