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Extraction and Adsorption Behavior of Co(II) on HTTA-Impregnated Polyurethane Foam

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ABSTRACT

The batch extraction of Co(II) from aqueous solutions with open cell polyether-type HTTA-loaded polyurethane (PU) foam has been studied using a radiotracer technique. The effect of pH, shaking time, and loading capacity has been investigated. The membrane properties of loaded PU foam sorbent offer unique advantage of adsorption. The fundamental studies of adsorption show that the classical Freundlich and Langmuir isotherms are followed in the entire concentration range of a 10^{-5} to 10^{-2} M solution of cobalt. The sorption mean free energy from the Dubinin–Radushkevich isotherm is found to be 13.8 kJ·mol^{-1} and the loading capacity 4.44 mg·g^{-1}, suggesting that the ion-exchange or chemisorption mechanism operates. The kinetic parameters of adsorption also support a chemisorption mechanism and the first-order rate law. The rate constants and activation energies of sorption and desorption have been evaluated. The thermodynamic function of adsorption of ΔH, ΔS, ΔG, and equilibrium constant K_C have been calculated. The process of adsorption is established to be endothermic and chemisorption, stabilized through thermodynamic functions.

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INTRODUCTION

The use of open cell polyurethane (PU) foam is a novel advancement in the field of preconcentration and separation science. Only a few systematic reviews of the potentiality of using PU foam in analytical separation have appeared (1–4), which suggest that open cell PU foam of the polyether type is a convenient substitute for liquid ethyl ether in an extraction system.

PU foam membrane can very easily immobilize hydrophobic organic and inorganic phases and facilitate the kinetics of the adsorption and extraction process in solid–liquid contact. Such organic reagents as dimethylglyoxime (5–7), diethyl dithiocarbamate (8, 9), and pyridylazonaphthol (10, 11) loaded on PU foam are widely used for the separation and preconcentration of trace elements from biotic and abiotic environmental samples (12–14).

The aim of this work is to demonstrate the use of reagent-loaded PU foam as a solid substance on which adsorption is also possible and to study the mechanism of adsorption by using different adsorption isotherms. The effect of temperature and the kinetics of the adsorption have also been investigated. In this work, 2-thenoyltrifluoroacetone (HTTA) has been selected as the loading reagent. As yet, no work has been reported with HTTA-loaded PU foam for the extraction and sorption of cobalt.

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EXPERIMENTAL

Reagents and Radiotracer

All reagents used in this work were Analar grade. Laboratory-grade 2-thenoyltrifluoroacetone (HTTA) from Fluka was used as obtained. Buffer solutions of pH 1 to 3 were prepared by mixing appropriate amounts of 0.2 M CH_3COONa, KCl, and HCl in different combinations; solutions of pH 4 to 6 were prepared using 0.2 M CH_3COOH and CH_3COONa. Buffers of pH 6 to 8 and 8.5 to 10 were prepared by mixing 0.2 M solutions of NaH_2PO_4 and NaOH, and solutions of H_3BO_3, NaCl, and NaOH, respectively. The ionic strength of all the buffer solutions was kept at 0.1 M by diluting with deionized water, and their stability was checked periodically.

The radiotracer of ^{60}Co was prepared by the irradiation of specpure metal in the PARR-1 reactor of the Pakistan Institute of Nuclear Science & Technology. The irradiated metal was dissolved in HNO_3, the contents were heated to dryness, and the final residue was dissolved in 1 mL of 0.1 M HNO_3 and diluted to 25 mL. Further dilutions were made from this solution. The radiochemical purity of the stock solution was checked through γ-spectrometry.

Apparatus/Instruments

All pH measurements were made with a Metrohm pH meter type 605. The shaking was performed in a 35 mL rectangular glass vial equipped with a screw-type polyethylene cap, whereas for studies at constant temperature, 25 × 125 mm Pyrex culture tubes with polyethylene screw caps were used.

Gross γ-ray measurements were made on a Tennelec counting assembly equipped with a well-type NaI(Tl) crystal. The radiochemical purity of the tracer was checked by a 25 cm^3 Ge(Li) detector coupled with a 4k series of 85 Canberra multichannel analyzer.

Foam Preparation

The PU foam used was an open-pore polyether type with a bulk density of 22 kg/m^3 supplied by a local firm. It was cut into cylindrical plugs of 5 mm diameter × 10 mm length for shaking purposes.

In order to remove all the organic and inorganic contaminations, the foam was first soaked in acetone for 30 minutes, pressed, then dried at 60°C. The dried foam was again squeezed in 2 M HCl for 2 hours followed by washing with deionized water till the washing was acid-free and neutral to alkaline phenolphthalein indicator. The washed foam was dried at 80°C for 2 hours and again squeezed with acetone for 30 minutes, pressed between filter paper, dried at 50°C, and stored for reagent loading.

The washed foam was squeezed first in 10% tributylphosphate (TBP) solution in acetone (as a plasticizer) for 30 minutes, dried in an oven at 80°C for 2 hours, and then again squeezed in 10% HTTA–acetone solution for 2 hours. The excess acetone was drained out, the foam was squeezed gently between two filter paper sheets to remove the excess HTTA–acetone solution, dried in the oven at 30°C, and stored in a prewashed and air-tight plastic bottle for further studies.

The amount of HTTA on the PU foam was determined by dissolving the HTTA-loaded PU foam in HPLC-grade methanol. The solution was run on a 830 Dupont Liquid Chromatogram. The loaded HTTA on PU foam was found to be 2.5% w/w, which was kept constant in all the experiments.

Procedure

The radiotracer of ^{60}Co was mixed uniformly with 5 mL of an aqueous solution of known pH in rectangular vials. A 1-mL aliquot was taken in a counting vial for gross γ-counts (A_0). To the remaining 4 mL of solution, two cylindrical plugs (30 mg) of HTTA-loaded PU foam were added and the contents were shaken on a wrist-action Griffin & George shaker for

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10 minutes or as required. After shaking, a 1-mL aliquot was assayed radiometrically (A_e).

For thermodynamics and kinetic studies, the radiotracer solution was taken in a culture tube and dipped in the Gallenkamp thermostirrer-100 model BKL 235 water bath for at least 30 minutes to attain the required temperature, and the same procedure was adopted for adsorption studies as described above. During shaking, about 70% of the length of the culture tube remained dipped in the water bath so that the solid–liquid contents were immersed completely in water of a controlled temperature.

The amount of cobalt adsorbed at any given temperature was calculated by the difference in the activity of the aliquots drawn before and after adsorption. The percentage extraction (% E) and distribution coefficient (K_D) are calculated as

$$\% E = \frac{A_0 - A_e}{A_0} \times 100$$

and

$$K_D = \frac{\text{amount of metal in foam}}{\text{amount of metal in solution}} \times \frac{\text{volume of solution}}{\text{weight of dry foam}} = (\text{mL/g})$$

Treatment of Data

There is no unique process which can explain the sorption mechanism of the hydrophobic complexes on PU foam. In general, several mechanisms including solvent extraction, ion exchange, clathration, and adsorption may be concomitantly involved (15).

The loading of the HTTA reagent on PU foam, denoted as $\overline{\text{TTA·Site}}$, and the adsorption of cobalt may be expressed as:

$$\text{Co}^{2+} + \overline{\text{TTA·Site}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{\text{Co·TTA·Site}} \qquad (1)$$

where k_1 and k_{-1} are the rate constants of adsorption and desorption, respectively. The overall rate constant, K', is calculated by the following equations:

$$K' = k_1(1 + 1/K_C) = k_1 + k_{-1}$$

and

$$K_C = k_1/k_{-1} \qquad (2)$$

where K_C is the equilibrium coefficient. From Eq. (1) at equilibrium, k_1 and k_{-1} can be correlated with the concentration of cobalt as

$$k_1/k_{-1} = C_{\text{ads}}/C_{\text{soln}} \qquad (3)$$

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where C_{ads} is the equilibrium concentration of cobalt on the adsorbent and C_{soln} is the equilibrium concentration of cobalt in solution. If F_θ is the fractional attainment of sorption at equilibrium, then

$$C_{soln} = C_0(1 - F_e) \tag{4}$$

and

$$C_{ads} = C_0 F_e \tag{5}$$

where C_0 is the initial concentration of cobalt in solution. By substituting the values of C_{ads} and C_{soln} from Eqs. (4) and (5) into Eq. (3), K_C becomes

$$K_C = F_e/(1 - F_e) \tag{6}$$

This shows that the equilibrium constant is independent of the weight of the sorbent and of the volume of the solution.

All the experiments were performed at least in triplicate at ambient temperature (23 ± 2°C) or as specified. A linear regression computer program with one independent variable was used for slope analysis, and standard formulas have been used for statistical treatment of the data (16–18).

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RESULTS AND DISCUSSION

The sorption of cobalt on HTTA-loaded polyurethane foam at different pHs is shown in Fig. 1 which indicates that the adsorption of a 1.1×10^{-5} M solution of Co(II) is maximum at pH 5.5 and remains constant up to pH 9. A slight decrease at pH 10 is due to the hydrolysis of Co(II). However, no sorption of Co(II) is found in the absence of HTTA on PU foam over the entire pH range studied.

The effect of shaking time (5 to 60 minutes) at pH 5.5 on the sorption of Co(II) is plotted in Fig. 2 which indicates that for a 1.1×10^{-5} M solution of Co(II), 10 minutes of shaking time is enough to attain equilibrium, but for a 1.2×10^{-3} M solution, a shaking time of 60 minutes is essential for attaining equilibrium, which remains constant up to 2 hours.

The loading isotherm of Co(II) ion from 10^{-5} to 10^{-2} M solution at pH 5.5 with 10 minutes of shaking time is plotted in Fig. 3, and it shows a gradual decrease of the sorption of Co(II) with an increase in its concentration. These results are in agreement with those shown in Fig. 2.

Adsorption Isotherms

To characterize the adsorption phenomena [i.e., physical or chemical adsorption of Co(II) on HTTA-loaded PU foam], several equations have been used to describe the data, especially when sorption is studied over

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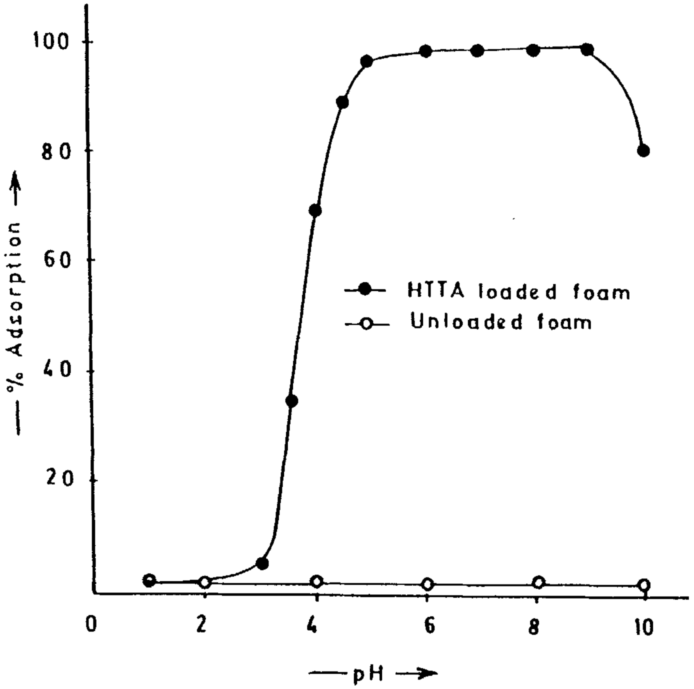

FIG. 1 Effect of pH on the sorption of Co(II) on polyurethane foam.

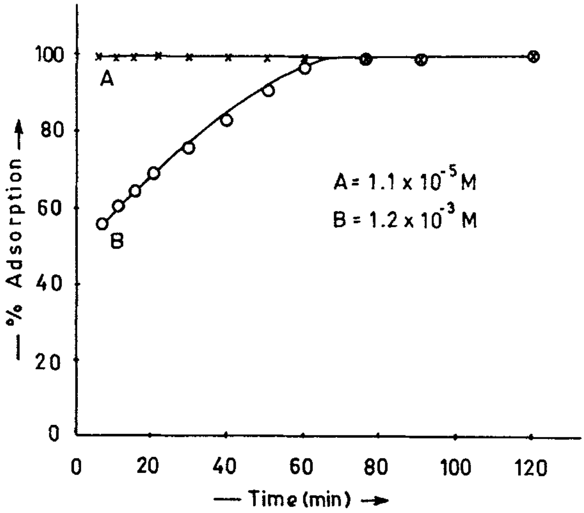

FIG. 2 Effect of shaking time on the sorption of Co(II) on HTTA-loaded polyurethane foam at pH 5.5.

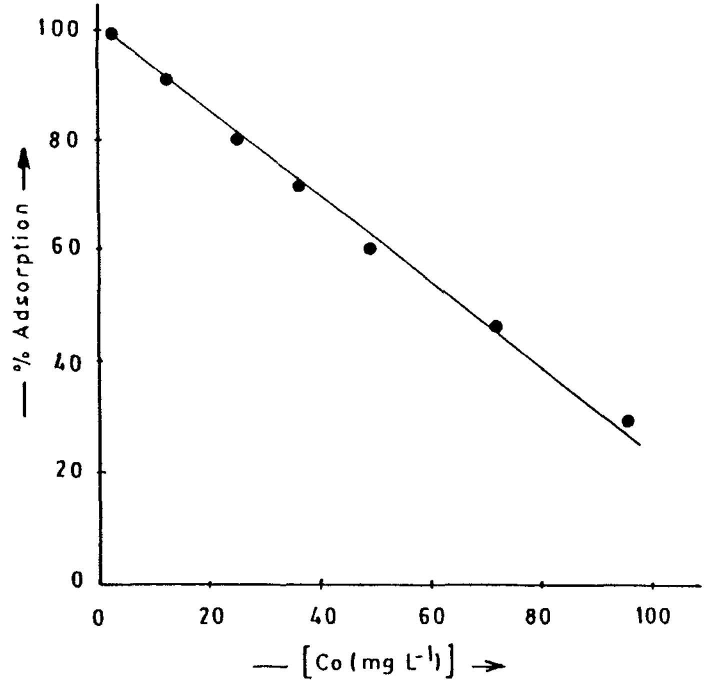

FIG. 3 Loading isotherm of Co(II) on HTTA-loaded polyurethane foam at pH 5.5. Shaking time: 10 minutes.

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a narrow range of concentration. The Freundlich (19) and Langmuir (20) isotherms are usually used. Although the Freundlich isotherm is regarded as empirical, there have been some attempts to get some information about surface heterogeneity from the empirical Freundlich constants. It often describes the trace amounts of adsorbed species satisfactorily. The linearized Freundlich equation is

$$\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_e \qquad (7)$$

where C_{ads} = amount of cobalt adsorbed (mol/g)
C_e = amount of cobalt in solution (mol/L)
A and $1/n$ = constants

The plot of log C_{ads} vs log C_e shown in Fig. 4 suggests that adsorption of Co(II) obeys the Freundlich isotherm over the entire range of the sorption concentration studied. The values of the constants A and $1/n$ are computed

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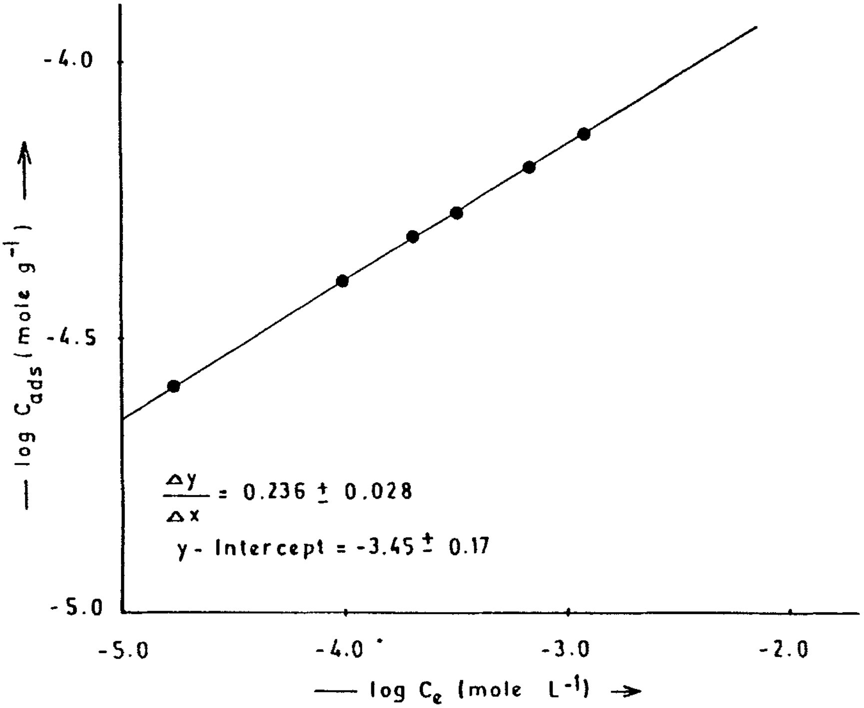

FIG. 4 Freundlich adsorption isotherm for Co(II) ions on HTTA-loaded polyurethane foam at pH 5.5.

from the slope and the intercept by means of a linear least-squares fit method and are given in Table 1. The $1/n$ value is usually dependent on the nature and strength of the adsorption process as well as on the distribution of the active sites. The low value of $1/n$ (0.24) clearly correspond to a heterogeneous surface with an exponential distribution of energy of the adsorption sites.

The Langmuir isotherm, generally recognized for monolayer and chemi-

TABLE 1
Different Constant Parameters of the Freundlich and Langmuir Isotherms

	A (mmol/g)	1/*n*	*M* (mg/g)	*b* (L/g)
Freundlich isotherm	0.35 ± 0.11	0.24 ± 0.03		
Langmuir isotherm			4.44 ± 0.21	0.26 ± 0.10

sorption, is written as

$$\frac{C_e}{C_{ads}} = \frac{1}{Mb} + \frac{C_e}{M} \tag{8}$$

where C_e = equilibrium cobalt concentration (mg/L)
C_{ads} = amount of cobalt adsorbed (mg/g)
M = constant related to maximum amount of solute adsorbed
b = constant related to the binding energy of the solute

A plot of C_e/C_{ads} vs C_e gives a straight line by using the least-squares technique, as shown in Fig. 5, confirming that this expression is indeed a reasonable representation of the chemisorption isotherm (21). The value of saturation capacity M is 4.44 mg/g, corresponding to monolayer coverage and therefore substantially independent of temperature, while b should vary with the temperature (22).

The adsorption data were also applied on another adsorption isotherm, the Dubinin–Radushkevich (23) isotherm, abbreviated as D–R. The D–R equation is

$$C_{ads} = C_m \exp(-B\epsilon^2) \tag{9}$$

where C_{ads} is the amount of cobalt adsorbed on HTTA-loaded PU foam, C_m is the maximum amount of cobalt that can be sorbed on HTTA-loaded PU foam under the optimized experimental conditions, B is a constant with a dimension of energy, and ϵ (Polyanyi potential) = $RT \ln(1 + 1/C)$, where R is the gas constant in $\mathrm{kJ \cdot K^{-1} \cdot mol^{-1}}$, T is the absolute temperature in °K, and C is the equilibrium concentration of cobalt in solution. This isotherm can be linearized into the slope–intercept form as

$$\ln C_{ads} = \ln C_m - B\epsilon^2 \tag{10}$$

When $\ln C_{ads}$ is plotted against ϵ^2, a straight line should result, as shown in Fig. 6. A linear regression by the method of least squares gave the values of C_m and B. If a very small subregion of the sorption surface is assumed to be uniform in structure and energetically homogeneous, and an approximation to the Langmuir isotherm is chosen as the local isotherm (24, 25), then the mean sorption energy (E) is given by

$$E = 1/\sqrt{-2B} \tag{11}$$

which is the free energy of transfer of 1 mole of solute from infinity (in solution) to the surface of the PU foam. The D–R parameters were evaluated for cobalt sorption on HTTA-loaded PU foam and are given in Table 2. The value of E (13.36 ± 0.37 kJ/mol) in the 8–16 kJ/mol range is ex-

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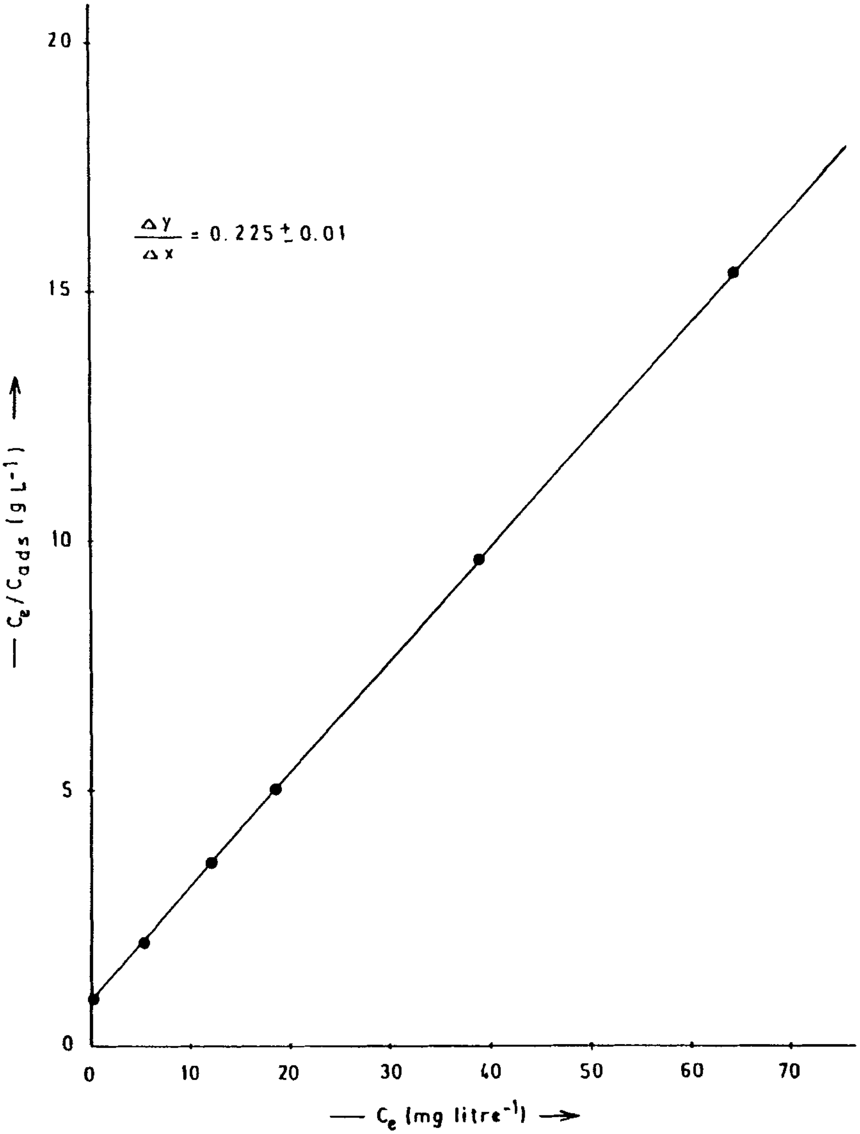

FIG. 5 Langmuir plot for chemisorbed Co(II) ions on HTTA-loaded polyurethane foam at pH 5.5.

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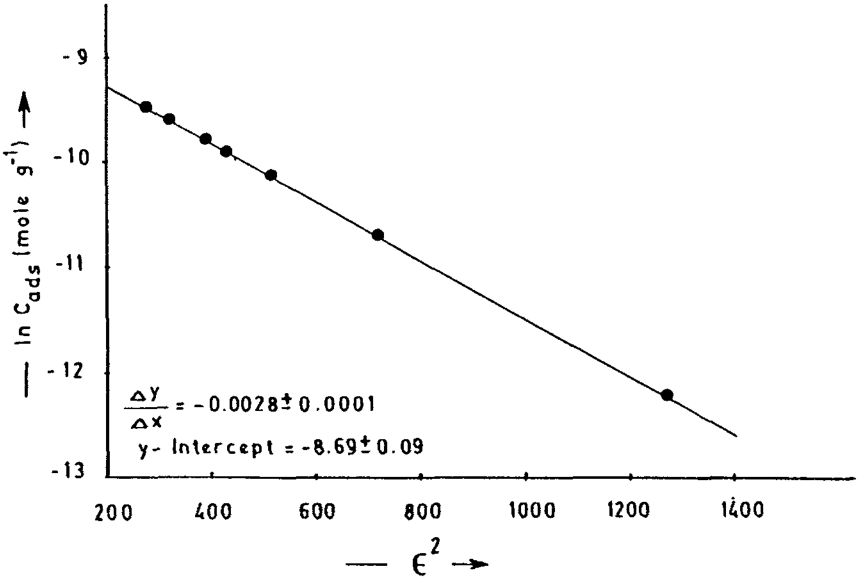

FIG. 6 Dubinin–Radushkevich (D–R) plot of cobalt adsorption on HTTA-loaded polyurethane foam.

TABLE 2
D–R Isotherm Parameters

	B (mol²/kJ²)	C_m (mmol·g^{-1})	E (kJ·mol^{-1})
D–R isotherm	−0.0028 ± 0.0001	0.168 ± 0.007	13.36 ± 0.37

pected for chemisorption or ion exchange (26). Hence, it is very likely that cobalt adsorbs on HTTA-loaded PU foam predominantly by chemisorption.

Kinetics

The kinetic data are interpreted either by diffusion or mass action transfer. The first interpretation of the kinetic data treats foam as porous particles of spherical shapes and assumes that cobalt diffuses into these micropores. The sorption of cobalt on HTTA-loaded PU foam may involve three steps: bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer, and diffusion of the solute within the pore volumes of the adsorbent and along pore–wall surfaces to active adsorption sites. Therefore, film and intraparticle transport are the major factors controlling rates of adsorption from solutions by porous adsorbents. Because K_D decrease with increasing cobalt concentration (Fig. 3), film diffusion does not seem to control the rate of sorption. Assuming that the time dependency of bulk sorption is governed by intraparticle diffusion, the equation given by Reichenberg (27) is as follows:

$$F = (1 - 6/\pi^2)e^{-Bt} \tag{12}$$

where

$$F = \frac{q_t}{q_e} = \frac{\text{amount of metal exchange after time } t}{\text{amount of metal exchange after infinite time}}$$

The value of Bt is a mathematical function of F and can be calculated for each value of F as

$$Bt = -0.4977 - \ln(1 - F) \tag{13}$$

Figure 7 shows that the plot of Bt vs t is linear but does not pass through the origin as predicted from Eqs. (12) and (13), showing that the particle diffusion mechanism is not operative and does not control the kinetics of cobalt sorption on HTTA-loaded PU foam.

Another equation in this regard, the Weber–Morris equation (28), as given below was also tested for kinetic data:

$$q_t = K_d\sqrt{t} \tag{14}$$

where q_t is the amount of cobalt adsorbed at time t.

The slope of the straight line of q_t vs $\sqrt{t}$ yields the value of K_d, the rate constant of intraparticle transport. The plot of q_t vs $\sqrt{t}$ (Fig. 8) is linear but does not pass through the origin. This observation was substantiated earlier by the fact that the data do not fit in the Reichenberg equation (Eq. 12), indicating that the sorption mechanism does not involve intraparticle diffusion.

Another way to interpret the kinetic data is by the mass-action process which assumes that solute adsorbs on the surface of the particle of foam according to a first-order reaction and that the time dependence is given by the Lagergren (29) equation in the form

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{15}$$

where q_e is the amount of cobalt adsorbed at equilibrium, q_t is the amount of cobalt adsorbed at time t, and k_1 is the rate constant of the sorption process.

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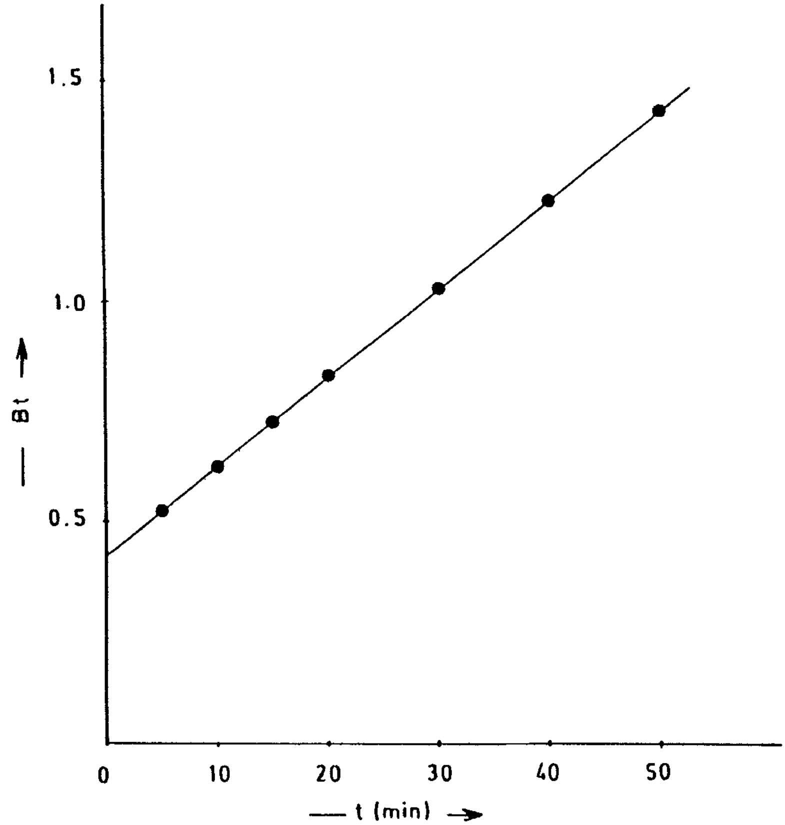

FIG. 7 *Bt* vs *t* plot of particle diffusion of cobalt on HTTA-loaded polyurethane foam at pH 5.5.

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A plot of $\log(q_e - q_t)$ vs t results in a straight line at the different temperatures studied, which indicates that the process is a first-order reaction with respect to the adsorbed concentration (30). The rate constants of adsorption calculated at different temperatures, taken from the slope of the linear plot of $\log(q_e - q_t)$ vs t, are recorded in Table 3. The rate constant of sorption increases from 0.14 to 0.225 min^{-1} with temperature, indicating that the adsorption of cobalt on HTTA-loaded PU foam is a chemical process rather than a physical one (31). The rate constant of desorption (k_{-1}) was also calculated using Eq. (3), and it is given in Table 3. The results indicate that adsorption of cobalt on HTTA-loaded PU foam is faster than desorption under similar experimental conditions.

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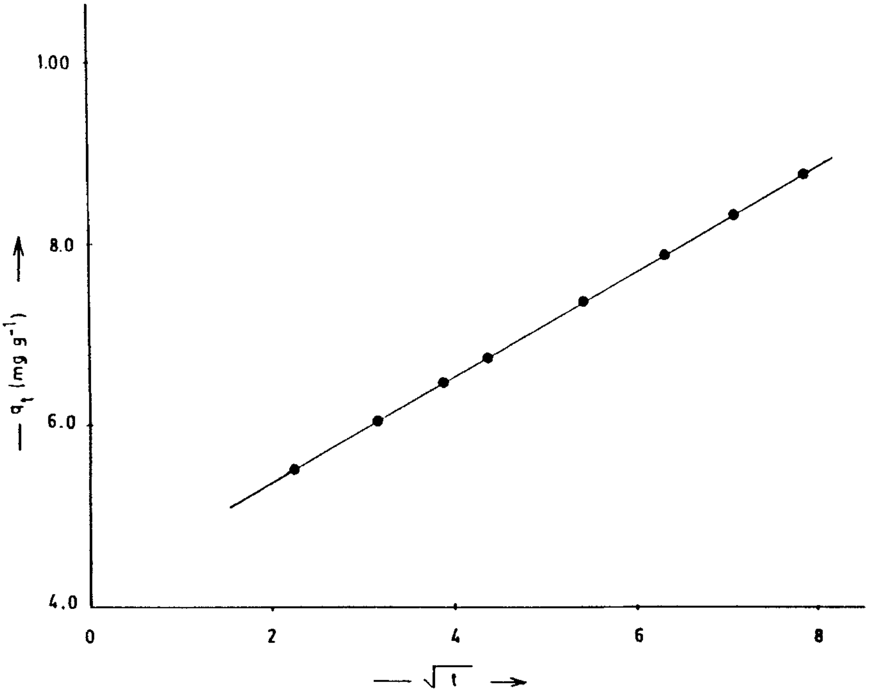

FIG. 8 Amount of cobalt adsorbed vs time$^{1/2}$ onto HTTA-loaded polyurethane foam.

TABLE 3
Kinetic Parameters for the Adsorption–Desorption Process of Co(II) on HTTA-Loaded Polyurethane Foam as a Function of Temperature[a]

Temperature (K)	Rate constant (min^{-1}) (k_1)	(k_{-1})	$K_C = k_1/k_{-1}$	Activation energy E_1 (kJ·mol^{-1})	E_{-1} (kJ·mol^{-1})
288	0.109	0.059	1.839	26.42 ± 0.77	−22.79 ± 0.58
293	0.135	0.052	2.606		
298	0.164	0.045	3.648		
303	0.194	0.038	5.053		
308	0.227	0.032	6.924		
313	0.262	0.028	9.395		

[a] Co(II) concentration = 8.4×10^{-5} M, pH 5.5

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The activation energy of sorption and desorption is also calculated using the Arrhenius equation:

$$\log k = \log A - E/2.303RT \tag{16}$$

where k is the rate constant and E is the activation energy of the reaction. The plots of $\log k_1$ and $\log k_{-1}$ vs $1/T$ are given in Fig. 9. From the slopes of the straight line representing sorption and desorption, the values of activation energies (E) have been calculated. They are summarized in Table 3. The negative value of the activation energy of the desorption process indicates that the reaction is endothermic and that desorption will decrease with a rise in temperature (32). The enthalpy (ΔH) of the adsorption and desorption processes was determined from the activation energies of sorption and desorption of cobalt on HTTA-loaded PU foam by using the relationship

$$\Delta H = E_{\text{ads}} - E_{\text{desor}} \tag{17}$$

The value of ΔH determined is $49.21 \pm 0.96\ \text{kJ}\cdot\text{mol}^{-1}$. The low activation energy of sorption as compared to the enthalpy indicates that the process

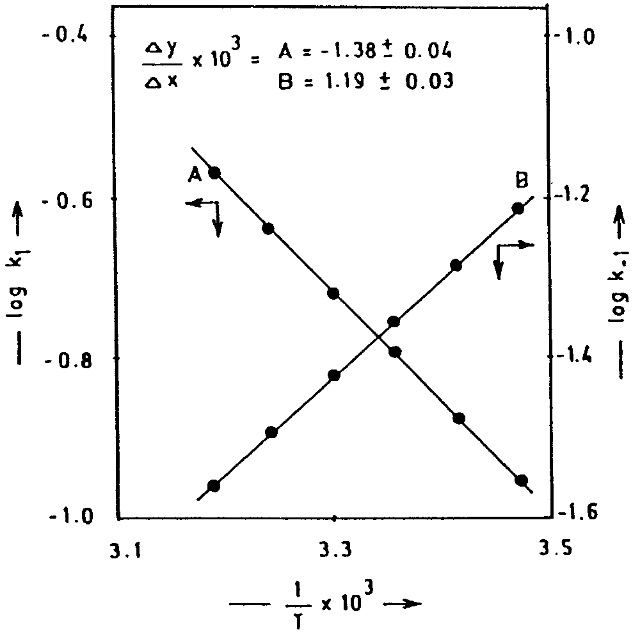

FIG. 9 Arrhenius plots for adsorption (k_1) and desorption (k_{-1}) of cobalt ions on HTTA-loaded polyurethane foam at pH 5.5.

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of attraction operating during sorption is strong, and that the uptake process can occur even under normal conditions. The increase of adsorbed concentration with temperature confirms that the process is chemisorptive in nature (33).

Thermodynamic Studies

The effect of temperature on the adsorption of Co(II) on HTTA-loaded PU foam was carried out by using the van't Hoff equation:

$$2.303 \log K_C = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{18}$$

where ΔH, ΔS, K_C, and T are the enthalpy, entropy, adsorption equilibrium constants, and temperature in Kelvins, respectively. R is a gas constant in $\mathrm{kJ \cdot K^{-1} \cdot mol^{-1}}$. The slope of a graph of $\log K_C$ vs $1/T$ is equal to $-\Delta H/R$, and the intercept is $\Delta S/R$. The main driving force of adsorption is Gibbs free energy (ΔG), which is calculated by using

$$\Delta G = \Delta H - T\Delta S \tag{19}$$

and

$$\Delta G = -RT \ln K_C \tag{20}$$

The values of K_D and K_C obtained at different temperatures are given in Table 4, which shows that they increase with an increase in temperature. The plot of $\log K_C$ vs $1/T$ is given in Fig. 10, and values of ΔH and ΔS calculated from the slope and intercept are given in Table 4.

The negative value of ΔG calculated from Eq. (20) indicates that the reaction is spontaneous and that the rate of adsorption is greater at higher temperatures than is the rate of desorption. The positive value of ΔH reflects that in the inner sphere complex of $\mathrm{Co(H_2O)_6^{2+}}$, the hydration

TABLE 4
Thermodynamic Parameters of the Adsorption of Co(II) on HTTA-Loaded Polyurethane Foam at pH 5.5

Temperature (K)	Distribution coefficient, K_D	Equilibrium constant, K_C	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS $(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$
288	245	1.839	−1.458	48.88	174.7
293	347	2.648	−2.333		174.7
298	486	3.648	−3.206		174.7
303	673	5.053	−4.081		174.7
308	923	6.924	−4.955		174.7
313	1252	9.395	−5.829		174.7

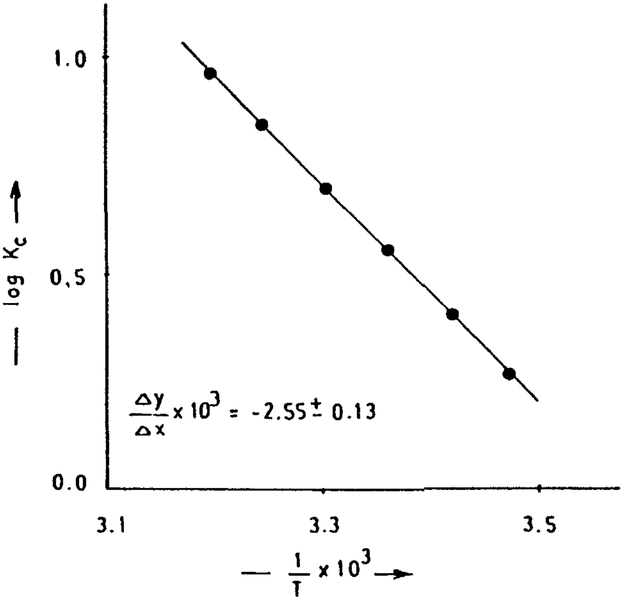

FIG. 10 Variation of K_C with $1/T$ at pH 5.5.

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zone is disrupted to a greater extent during adsorption, which results in a net endothermic enthalpy change. The positive ΔS value reveals that elimination of the hydration zone during adsorption of cobalt on HTTA-loaded PU foam results in a net positive entropy effect (34). The data show that the removal of the hydrated water molecules around the central metal atom is only carried out by chemisorption or by a strong interaction of HTTA and cobalt on PU foams.

The data presented here are useful for the derivation of the sorption mechanism on reagent-loaded PU foam. These data are also helpful for the preconcentration and separation of cobalt from radioactive waste and its monitoring at trace and ultratrace levels from such aqueous solutions as drinking water and seawater.

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