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# Cation-exchange kinetics for various metal ions and thermodynamics studies for the adsorption of mancozeb pesticide on ployaniline Sn(IV) phosphate cation-exchanger

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## ABSTRACT

Ion-exchange kinetics on an electrically conducting organic-inorganic composite cation-exchanger have been studied for $Mg^{2+}$-$H^+$, $Ca^{2+}$-$H^+$, $Sr^{2+}$-$H^+$, $Ba^{2+}$-$H^+$, $Ni^{2+}$-$H^+$, $Cu^{2+}$-$H^+$, $Mn^{2+}$-$H^+$ and $Zn^{2+}$-$H^+$ exchanges at 25,33,50 and 65($\pm$0.5)$^0$C temperatures using approximated Nernst-Plank equation under the particle diffusion controlled phenomenon. In this consequent some physical parameters, i.e., fractional attainment of equilibrium $U(\tau)$, self-diffusion coefficients ($D_0$), energy of activation ($E_a$), and entropy of activation ($S^*$) have been determined. The adsorption thermodynamic for the adsorption of mancozeb, a fungicide of the class ethylenebisdiothiocarba mate have also been demonstrated on the surface of this composite cation-exchanger at 25,35,45$^0$C. As a result some thermodynamic parameters like Freundlich constants, thermodynamic equilibrium constants($K_0$), standard free energy changes ($\Delta G°$), and standard enthalpy change($\Delta H°$) and standard entropy changes ($\Delta S°$) have been evaluated.

## KEYWORDS

Organic-inorganic composite material;
Cation-exchanger;
Ion-exchange kinetics;
Adsorption thermodynamics;
Pesticide mencozeb.

## INTRODUCTION

Polyaniline Sn(IV) phosphate an electrically conducting composite cation-exchanger has been studied for the synthesis, physico-chemical characterization, ion-exchange properties and electrical conductivity measurements[1]. On account of ion-exchange properties this cation-exchanger possessed a better ion-exchange capacity 1.96 meq dry $g^{-1}$ as compared to inorganic cation-exchanger Sn(IV) phosphate i.e. 1.12 meq dry $g^{-1}$ and high selectivity for mercury a toxic metal ion. To explore the analytical utility of the cation-exchange material a mercury selective ion-sensitive membrane electrode was developed and used for analytical studies[2]. However, the ion-exchange mechanism of the cation-exchanger has yet to be determined. Therefore, kinetic studies of the exchange of some divalent alkali and transition metal ions have been conducted to understand the mechanism of ion-exchange and its separation potential on the surface of the material. In view of aforesaid facts, investigations of some kinetic parameters such as the diffusion coefficient, energy and entropy of activation, etc., are important. It is noteworthy that these parameters tell us about the mechanism, rate determining step and rate laws obeyed by the ion-exchange process. Moreover, the earlier approaches[3-6] of kinetic behavior are based on the old Bt criterion[7,8], which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities[9] of the exchanging ions involved. The Nernst-Planck [10,11] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely[12-19].

The presence of an ion-exchange material possessing a good ion-exchange capacity may enhance the adsorption characteristics of the soil. The adsorption of pesticides on soils has been a significant feature[20,21]. It is affected by the presence of metal ions, which play an important role in modifying the nutritional status of the soils. Inorganic ion-exchangers are known to be selective for metal ions and hence their presence in soil may have some far reaching consequences[22,23]. They could effect a greater retention of metal ions in soil owing to their ion-exchange behavior, thus preventing them from entering into crops and ultimately to the food chain. These materials have been found to adsorb pesticides to a much greater extent than the ordinary soils, for example antimony(V) silicate[24] prepared in these laboratories has shown about a ten-fold enhanced adsorption potential for the pesticide carbofuran as compared to soils. In order to extend such a study, this cation-exchanger was also selected for the adsorption of pesticide. The adsorption properties on polyaniline Sn(IV) phosphate was observed for the adsorption of mancozeb which is a member of ethylenebisdiothiocarbamate (EBDC) fungicides. Mancozeb is used to protect many fruit, vegetable, nut and field crops against a wide spectrum of fungal diseases, including potato blight, leaf spot, scab (on apples and pears), and rust (on roses). It is also used for seed treatment of cotton, potatoes, corn, sunflower, sorghum, peanuts, tomatoes, flax, and cereal grains. Mancozeb is available as dusts, liquids, water dispersible granules, as wettable powders, and as ready-to-use formulations. It may be commonly found in combination with zineb and maneb. It is an organophosphate compound used commonly as an insecticide in agricultural, household and public health uses to control different types of insects.

## EXPERIMENTAL

### 1. Reagents and instruments

The reagents used were obtained from CDH, E-Merck and Qualigens (India Ltd.). A water bath incubator shaker having a temperature variation of ± 0.5$^0$C was used for all equilibrium studies. An electronic balance (digital), Sartorius (Japan), model 21 OS was used for weighing purpose.

### 2. Preparation of reagents

Mancozeb suspension of different molarities ranging from 0.01-0.06M was prepared in demineralized water (DMW). 0.1N iodine solution was prepared in potassium iodide followed by DMW. 10% lead acetate solution was prepared in MDW and 2N potassium hydroxide in methanol.

### 3. Preparation of polyaniline Sn(IV) phosphate

Polyaniline Sn(IV) phosphate composite cation-exchanger was prepared as reported earlier[1]. The organic polymer polyaniline was prepared by mixing equal volumes of the solution of 10% aniline ($C_6H_5NH_2$) and 0.1M potassium persulphate ($K_2S_2O_8$) prepared in 1M HCl with continuous stirring by a magnetic stirrer for half an hour at 0$^0$C, and green colored gel was obtained. The gel was transferred into the white precipitate of Sn(IV) phosphate prepared at room temperature (25±2$^0$C) and at pH=1 by adding 0.1M stannic chloride solution to an aqueous solution of 0.1M disodium hydrogen orthophosphate ($Na_2HPO_4$) in 2:3 ratio. The resultant green colored gel was kept for 24h at room temperature (25±2$^0$C) for digestion. The supernatant liquid was decanted and the gel was filtered by suction. The excess acid was removed by washing with demineralized water (DMW) and the material was dried in an air oven at 50$^0$C. The dried product was immersed in DMW to obtain small granules. They were converted to $H^+$-forms by treating with 1M $HNO_3$ for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and finally dried at 50$^0$C. The particles size of ~125μm of the material was obtained by sieving and kept in desiccators. The ‘polyaniline Sn(IV) phosphate’ composite cation-exchanger possessed 1.96 meq dry g$^{-1}$ of the

**TABLE 1 : Conditions of preparation and the ion-exchange capacity of polyaniline Sn(IV) phosphate composite cation-exchange material**

| Sample | Mixing volume ratio | | | | | Appearance of beads after drying | $Na^+$ ion-exchange capacity (meq dry $g^{-1}$) |
|---|---|---|---|---|---|---|---|
| | M $SnCl_4.5H_2O$ in 4M HCl | 0.1M $Na_2HPO_4$ in DMW | pH of the inorganic precipitate | 0.1M $K_2S_2O_8$ in 1M HCl | 10% Aniline in 1 M HCl | | |
| S-1 | 2 | 3 | 1.0 | 1 | 1 | Greenish granular | 1.96 |
| S-2 | 2 | 3 | 1.0 | - | - | White granular | 1.12 |

$Na^+$ ion-exchange capacity. The conditions of preparation and ion-exchange capacity are given in TABLE 1.

## 4. Kinetic measurements

The composite cation-exchange material was treated with 0.5M $HNO_3$ for 24h at room temperature with occasional shaking; intermittently replacing the supernatant liquid with a fresh acid to ensure the complete conversion to $H^+$-form and the excess acid was removed after several washing with DMW. Now the dried ion-exchanger sample in the $H^+$-form was grounded and then sieved to obtain particles of definite mesh sizes (25-50, 50-70, 70-100 and 100-125μm). Out of them the particles of mean radii ~125μm (50-70 mesh) were used to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

Twenty-milliliter fractions of the 0.02M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200mg of the cation-exchanger in $H^+$-form in several stoppered conical flasks at desired temperatures [25,33,50 and 65(±0.5)$^0$C] for different time intervals (0.5, 1.0, 2.0, 3.0 and 4.0 min.). The supernatant liquid was removed immediately and determinations were made usually by EDTA titrations[25]. Each set was repeated four times and the mean values were taken for calculations.

## 5. Adsorption thermodynamics

A total of 0.5 g portions of the polyaniline Sn(IV) phosphate composite cation-exchanger were placed in various stoppered conical flasks at the desired temperatures (25, 35 and 45$^0$C) followed by the addition of 10 ml mancozeb suspensions of different concentrations varying from 0.01-0.06M and the mixtures were shaken for 70 min, each to attain equilibrium. The concentrations of mancozeb before and after adsorption were analyzed by iodometrically as given below.

## 6. Traditional $CS_2$ reaction system

The system proposed by Cullen[26] consists of a two-necked round bottom flask connected to a condenser, which is connected to two traps in series. $CS_2$ formed after hydrolysis of mancozeb taken in round bottom flask carrying into the first trap containing lead acetate [$Pb(CH_3COO)_2$] solution to aid in the removal of interferences. After that $CS_2$ is reacted with methanolic KOH present in the second trap and the xanthate formed is titrated with $I_2$ solution.

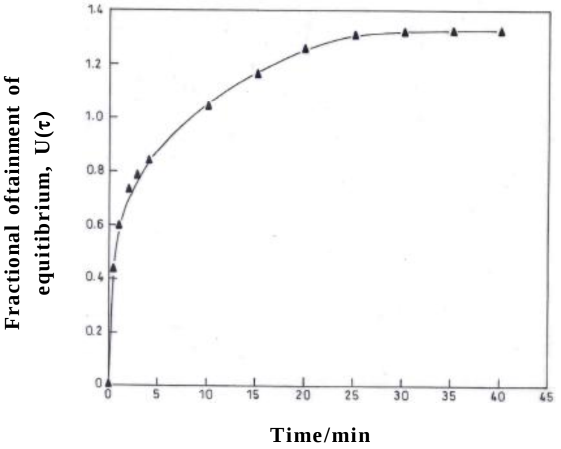

**Figure 1 : A plot of U(τ) versus t (time) for M(II)-H(I) exchanges at 33$^o$C on polyaniline Sn(IV) phosphate composite cation-exchanger for the determination of infinite time**

## RESULTS AND DISCUSSIONS

## 1. Cation-exchange kinetics of metal ions

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I), Ba(II)-H(I), Ni(II)-H(I), Cu(II)-H(I), Mn(II)-H(I) and Zn(II)-H(I). The particle diffusion-controlled phenomenon was favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

The infinite time of exchange was the time necessary to obtain equilibrium in an ion exchange process. The ion-exchange rate became independent of time af-

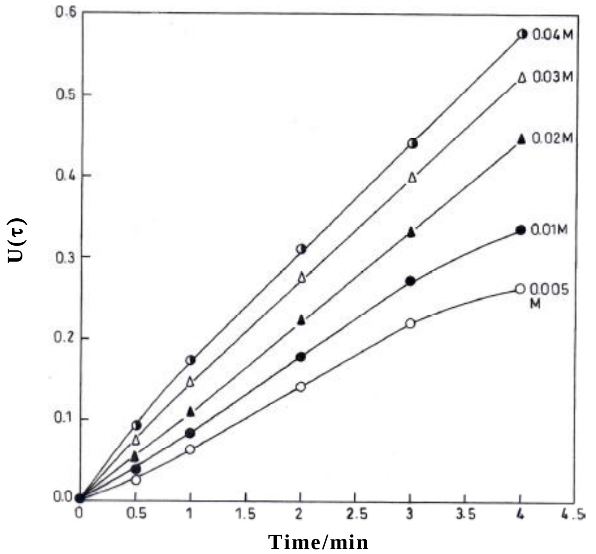

**Figure 2 : Plots of $U(\tau)$ versus t (time) for M(II)-H(I) exchanges using different metal solution concentrations at 33°C on polyaniline Sn(IV) phosphate composite cation-exchanger**

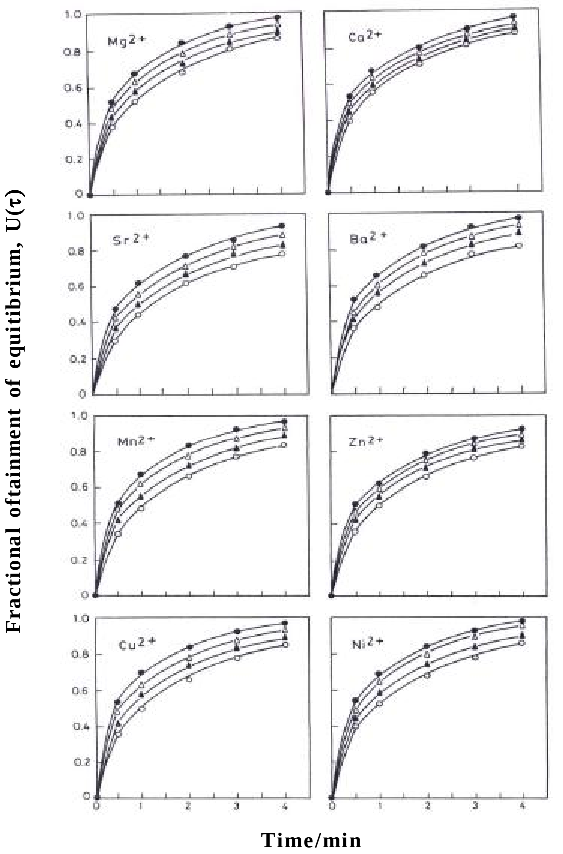

**Figure 3 : Plots of $U(\tau)$ versus t (time) for different M(II)-H(I) exchanges at different temperatures on polyaniline Sn(IV) phosphate composite cation-exchanger: (□) 25°C, (▲) 33°C, (Δ) 50°C, (●) 65°C**

ter this interval. Figure 1 showed that 25min. were required for the establishment of equilibrium at 33°C for $Mg^{2+}$-$H^+$ exchange. Similar behavior was observed for $Ca^{2+}$-$H^+$, $Sr^{2+}$-$H^+$, $Ba^{2+}$-$H^+$, $Ni^{2+}$-$H^+$, $Cu^{2+}$-$H^+$, $Mn^{2+}$-$H^+$ and $Zn^{2+}$-$H^+$ exchanges. Therefore, 25 min was assumed to be the infinite time of exchange for the system. A study of the concentration effect on the rate of exchange at 33°C showed that the initial rate of exchange was proportional to the metal ion concentration at and above 0.02M(Figure 2). Below the concentration of 0.02M, film diffusion control was more prominent.

The results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation:

$$U(\tau) = \text{the amount of exchange at time 't'} / \text{the amount of exchange at infinite time} \qquad (1)$$

Plots of $U(\tau)$ versus time (t) (t in min.), for all metal ions (Figure 3) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature and the uptake decreased with time. Each value of $U(\tau)$ will have a corresponding value of $\tau$, a dimensionless time parameter. On the basis of the Nernst-Planck equation, the numerical results can be expressed by explicit approximation[27-29]:

$$U(\tau) = \{1 - \exp[\pi^2 (f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \qquad (2)$$

where $\tau$ is the half time of exchange = $\bar{D}_{H^+} t / r_o^2$, $\alpha$ is the mobility ratio = $\bar{D}_{H^+} / \bar{D}_{M^{2+}}$, $r_o$ is the particle radius, $\bar{D}_{H^+}$ and $\bar{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions $H^+$ and $M^{2+}$ respectively, in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio ($\alpha$) and the charge ratio ($Z_{H^+}/Z_{M^{2+}}$) of the exchanging ions. Thus they have different expressions as given below. When the exchanger is taken in the $H^+$-form and the exchanging ion is $M^{2+}$, for $1 \leq \alpha \leq 20$, as in the present case, the three functions have the values-

$$f_1(\alpha) = -1 / 0.64 + 0.36\,\alpha^{0.668}$$
$$f_2(\alpha) = -1 / 0.96 - 2.0\,\alpha^{0.4635}$$
$$f_3(\alpha) = -1 / 0.27 + 0.09\,\alpha^{1.140}$$

The value of $\tau$ is obtained on solving equation (2) using a computer. The plots of $\tau$ versus time (t) at the four temperatures, as shown in figure 4, are straight lines passing through the origin, confirming the particle

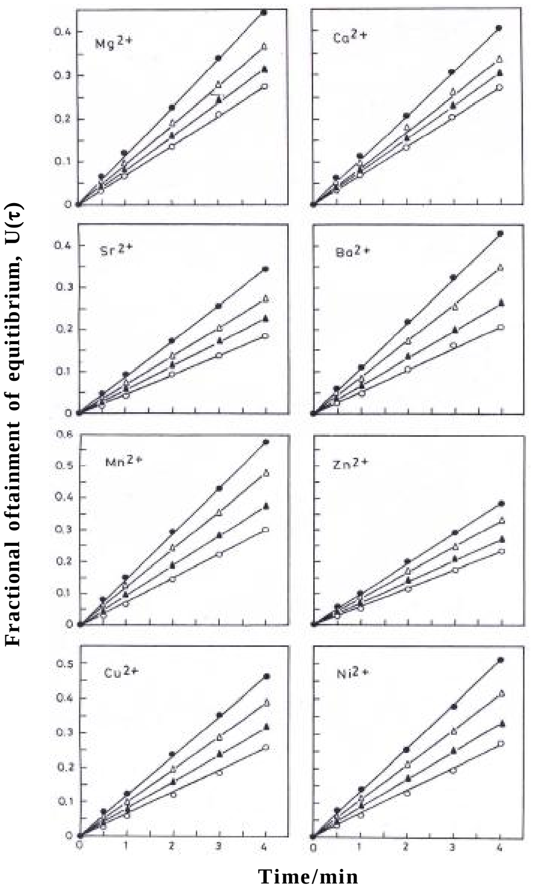

**Figure 4 : Plots of τ versus t (time) for different M(II)-H(I) exchanges at different temperatures on polyaniline Sn(IV) phosphate composite cation-exchanger: (□) 25°C, (▲) 33 °C, (Δ) 50°C, (●) 65°C**

diffusion control phenomenon for M(II)-H(I) exchanges at a metal ion concentration of 0.02M.

The slopes (S values) of various τ versus time (t) plots are given in TABLE 2. The S values are related to $\bar{D}_{H^+}$ as follows:

$$S = \bar{D}_{H^+} / r_0^2 \qquad (3)$$

The values of –log $\bar{D}_{H^+}$ obtained by using equation (3) plotted against 1/T are straight lines as shown in figure 5, thus verifying the validity of the Arrhenius relation:

$$\bar{D}_{H^+} = D_0 \exp(-E_a/RT) \qquad (4)$$

$D_0$ is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy ($E_a$) is then calculated with the help of the equation (4), putting the value of $\bar{D}_{H^+}$ at 273K. The entropy of activation (ΔS*) was then calculated by substituting $D_o$ in equation (5).

**TABLE 2: Slopes of various τ versus time (t) plots on polyaniline Sn(IV) phosphate cation-exchanger at different temperatures**

| Migrating ions | S ($s^{-1}$) × $10^2$ | | | |
|---|---|---|---|---|
| | 25°C | 33°C | 50°C | 65°C |
| Mg(II) | 6.83 | 7.83 | 9.18 | 11.18 |
| Ca(II) | 6.72 | 7.58 | 8.51 | 10.15 |
| Sr(II) | 4.56 | 5.63 | 6.79 | 8.58 |
| Ba(II) | 5.31 | 6.65 | 8.63 | 10.77 |
| Cu(II) | 6.28 | 7.84 | 9.59 | 11.61 |
| Ni(II) | 6.60 | 8.25 | 10.32 | 12.70 |
| Zn(II) | 5.79 | 6.76 | 8.29 | 9.70 |
| Mn(II) | 7.40 | 9.29 | 11.87 | 14.36 |

**TABLE 3: Values of $D_0$, $E_a$ and ΔS* for the exchange of H(I) with some metal ions on polyaniline Sn(IV) phosphate composite cation-exchange material**

| Metal ion exchange with H(I) | $10^9$Ionic mobility /$m^2 V^{-1} s^{-1}$ | $10^2$Ionic radii / nm | $10^7D_0$ /$m^2 s^{-1}$ | $10^2E_a$/kJ $mol^{-1}$ | ΔS*/J$K^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|
| Mg(II) | 55 | 7.8 | 1.88 | 68.24 | - 0.39 |
| Ca(II) | 62 | 10.6 | 2.57 | 74.53 | - 0.26 |
| Sr(II) | 62 | 12.7 | 1.36 | 67.92 | - 0.53 |
| Ba(II) | 66 | 14.3 | 2.79 | 74.95 | - 0.22 |
| Cu(II) | 57 | 7.0 | 1.16 | 61.04 | - 0.60 |
| Ni(II) | 52 | 7.8 | 1.55 | 63.92 | - 0.48 |
| Zn(II) | 56 | 8.3 | 0.80 | 57.81 | - 0.78 |
| Mn(II) | 55 | 9.1 | 2.27 | 67.60 | - 0.31 |

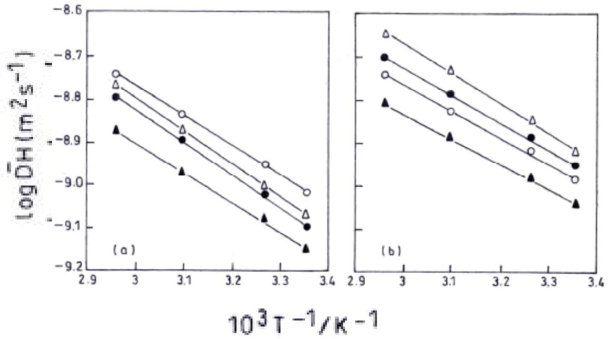

**Figure 5 : Plots of –log $D_H$ versus 1000/T (K) for (a) Mg (II): □, Ca(II): ●, Ba(II): Δ, Sr(II): ▲, and (b) Mn(II): Δ, Ni(II): ●, Cu(II):? □, Zn(II): ▲, on polyaniline Sn(IV) phosphate composite cation-exchanger**

$$D_0 = 2.72 d^2 (kT / h) \exp(\Delta S^*/R) \qquad (5)$$

where d is the ionic jump distance taken as 5×$10^{-10}$m, k is the Boltzmann constant, R is the gas constant, h is Plank's constant and T is taken as 273 K. The values of the diffusion coefficient ($D_o$), energy of activation ($E_a$) and entropy of activation (ΔS*) thus obtained are summarized in TABLE 3.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Figure 3), probably because of a higher diffusion rate of ions through the ther-

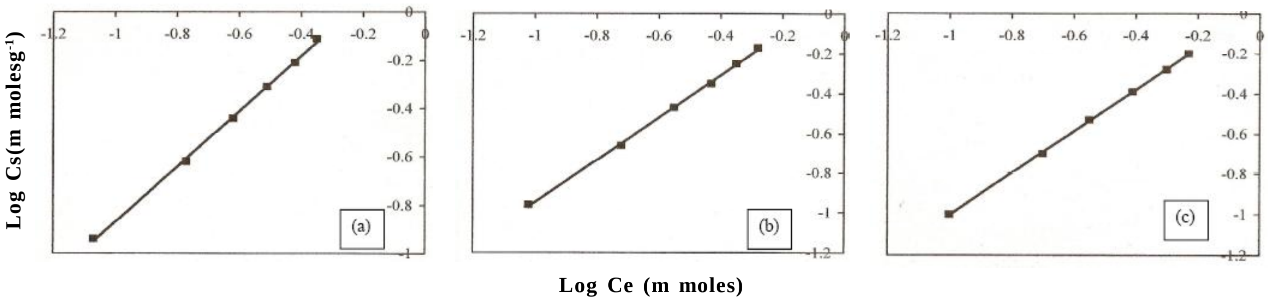

Figure 6 : Freundlich isotherm of mancozeb adsorption on polyaniline Sn(IV) phosphate at 25°C (a), 35°C (b) and 45°C (c)

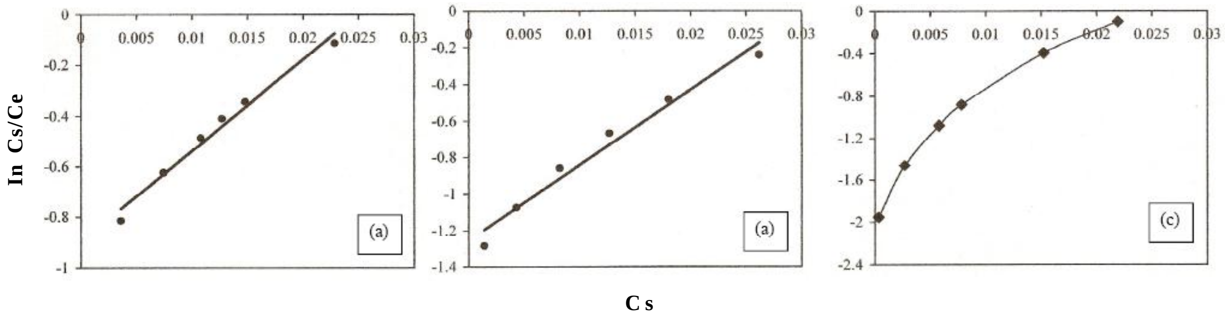

Figure 7 : Plots of ln Cs/Ce versus Cs on polyaniline Sn(IV) phosphate composite cation exchanger at 25°C (a), 35°C (b) and 45°C (c)

**TABLE 4: Freundlich isotherm constants K and 1/n for the adsorption of mancozeb on polyaniline Sn(IV) phosphate composite cation-exchanger**

| Freundlich constant | Temperature (°C) | | |
|---|---|---|---|
| | 25 | 35 | 45 |
| *K* | 0.82 | 0.57 | 0.85 |
| 1/n | 1.58 | 1.51 | 1.67 |

**TABLE 5: Values of various thermodynamic parameters for the adsorption of mancozeb on polyaniline Sn(IV) phosphate composite cation-exchanger**

| Thermodynamic constan | Temperature (°C) | | |
|---|---|---|---|
| | 25 | 35 | 45 |
| $K_\alpha$ | 1.2536 | 1.2534 | 1.1963 |
| $\Delta G°$(K cal mol$^{-1}$) | - 0.1336 | - 0.1380 | - 0.1131 |
| $\Delta H°$(K cal mol$^{-1}$) | - 0.58 | - 0.58 | - 0.58 |
| $\Delta S°$(K cal mol$^{-1}$deg$^{-1}$) | $2.3551\times10^{-3}$ | $1.4351\times10^{-3}$ | $-1.4682\times10^{-3}$ |

mally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the $\tau$ versus time (t) plots, as shown in Figure 4. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange [M(II) - H(I)] process.

## 2. Adsorption thermodynamics of mancozeb

The adsorption isotherms at 25, 35 and 45$^0$C, follow adequately a Freundlich adsorption behavior and can be represented by the equation:

$$x/m = KC^{1/n} \quad (6)$$

where x/m is the surface concentration of mancozeb in millimoles per gram of the exchanger represented as Cs, C is the equilibrium concentration of mancozeb (m mol ml$^{-1}$) represented as Ce, and K and 1/n are constants.

According to this equation plots of log Cs versus log Ce are straight lines at desirable temperatures (Figure 6), and K and 1/n are the constants determined from the intercepts and slopes of the starting lines, respectively, fitted to the points by the least squares method. The values obtained are listed in TABLE 4.

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant $K_o$ (or the thermodynamic coefficient) with the change in temperature. The constant, $K_o$ for the adsorption reaction can be defined as follows:

$$K_o = a_s / a_e = v_s C_s / v_s C_e \quad (7)$$

where $a_s$ is the activity of adsorbed solute, $a_e$ is the activity of the solute in solution at equilibrium, $C_s$ is the surface concentration of mancozeb in m mol per gram of exchanger, $C_e$ is the concentration of mancozeb at equilibrium (m mol ml$^{-1}$), $\nu_s$ is the activity coefficient of the adsorbed solute and $\nu_e$ is the activity coefficient of the solute in solution.

As the concentration of the solute in the solution approaches zero, the activity coefficient approaches unity, reducing Eq. 7 to the following form-

$$K_o = a_{s/}a_{e=}C_s / C_e \qquad (8)$$

Values of $K_o$ are obtained by plotting ln $(C_s/C_e)$ versus $C_s$ (Figure 7) and extrapolating $C_s$ to zero [20]. The straight line obtained is fitted to the points based on a least squares analysis. Its intercept with the vertical axis gives the values of $K_o$. Standard free energy changes (ΔG°) for interactions are calculated[30] from the relationship:

$$\Delta G° = -RT \ln K_o \qquad (9)$$

where R is the universal gas constant and T is the temperature in Kelvin. The average standard enthalpy change (ΔH°) is then calculated from the well-known Van't Hoff equation:

$$\ln K_0(T_3) - \ln K_0(T_1) = -\Delta H° (T_1 \text{ to } T_3)/R(1/T_3 - 1/T_1) \qquad (10)$$

where $T_3$ and $T_1$ are two different temperatures. Standard entropy changes (ΔS°) are calculated using the equation

$$\Delta G° = \Delta H° - T\Delta S° \qquad (11)$$

The values obtained are given in TABLE 5. A negative value of the standard enthalpy change indicates the mancozeb-exchanger interaction is exothermic. It is supported by the adsorption of mancozeb decreases with the increase in temperature. Since the free energy changes are negative and accompanied by a positive entropy changes, the reactions are spontaneous with a high affinity for mancozeb[31].

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