

## KINETICS AND MECHANISM OF EXCHANGE SORPTION OF Fe(III) IN AQUEOUS AND AQUEOUS-ORGANIC MEDIA

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### Abstract

Studies have been made on the kinetics and mechanism of exchange sorption of Fe(III) on m-cresol-phenol formaldehyde (H<sup>+</sup>-from), using modified limited batch technique in aqueous and aqueous-isopropanol media. The sorption of Fe(III) was found to be markedly affected by the change of dielectric constant of all the systems studied here in. Using an equation of the Arrhenius type  $D_i/D_0 = \exp^{-E_a/RT}$ , the values of activation energies were found to be 3.71 , 3.56 , 3.31 and 3.08 K cal/mole in case of 0.0 , 30.60 and 80% (v/v) isopropanol respectively. The increase in the exchange rate with decreasing resin particle size (0.031-0.022 cm) and with increasing the temperature (25-60 °c) has been discussed. Diffusion of ferric ion through the solid phase is found to be the rate-determining step in the exchange process. The negative values of  $\Delta S^*$  have been taken as indicative of a comparatively higher degree of mobility and the lack of an orientational effect.

### Introduction

Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution, and stirring velocity on the sorption of Cd(II) and Pb(II) by sawdust of *P. sylvestris*[1]. Kinetic aspects are studied in order to develop a model which can describe the process of adsorption on sawdust. The equilibrium of a solution between liquid and solid phases is described by Langmuir model. Scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) shows that the process is controlled by a porous diffusion with ion-exchange. The capacity of the metal ions to bind onto the biomass was 96% for Cd(II), and 98% for Pb(II). The sorption followed a pseudo-second-order kinetics. The adsorption of these heavy metals ions increased with the pH and reached a maximum at 5.5 value. From these results, it can be concluded that the sawdust of *P. sylvestris* could be a good adsorbent for the metal ions coming from aqueous solutions. Moreover, this material could also be used for purification of water before rejection into the natural environment.

An algal industrial waste from the agar extraction process was immobilized with an organic polymer (polyacrylonitrile, PAN) and used as a biosorbent for Pb(II) removal from aqueous solutions[2]. The effects of the initial concentration, stirring velocity and particles diameter on Pb(II)

biosorption were investigated in a batch system in order to explain the adsorption mechanism. Uptake kinetics follows the second-order Lagergren model and equilibrium is well described by the Langmuir isotherm. Maximum biosorption capacity of the composite material was found to be  $\approx 20$  mg Pb(II) g. Kinetic constants vary with the initial metal concentration. The adsorptive behaviour of biosorbent particles was modeled using a batch reactor mass transfer kinetic model. The homogeneous diffusion coefficient for particles with diameter 0.5 – 1 mm and for an initial concentration of 94 mg Pb(II) solution was found to be  $3.2 \times 10^{-8}$  cm s<sup>-1</sup>.

Misra[3] have been applied the Nernst-Planck equations to study the ion exchange kinetics on the surface of zirconium(IV) phosphoantimonate for Mg(II)-H(I), Sr(II)-H(I) and Ba(II)-H(I) exchanges under conditions favouring a particle diffusion coefficient, energy of activation and entropy of activation have been evaluated. The energy and entropy of activation vary linearly with the ionic radii and mobilities.

A new chelating resin based on a phenol-formaldehyde copolymer containing diethylene triamine pentaacetic acid (DTPA) as a function species has been synthesized by Singh and Gupta[4]. They have been studied capacity and sorption kinetics. The complexation ability of the sorbent towards 19 metal ions has been studied. The resin may success fully be applied to the selective separation and recovery of some metal ions.

The present work is an attempt to study the kinetics and mechanism of the exchange process of Fe(III)/H(I) ion with the aim to obtain informations about the rate-determining step of the ion exchange process by varying the polarity of the studied systems using different proportions ( 0.0 , 30 , 60 and 80% (v/v)) of isopropanol-water systems. The study was performed at different temperatures (25 , 40 and 60 °c ) using two particle sizes ( 0.022 and 0.031 cm ) of the cation exchanger. Experiments on batch contact for metal ion uptake and F(III)/H(I) interdiffusion were carried out to help in the understanding of the ions intraparticle motion.

## Experimental

Ferric chloride, isopropanol, hydrochloric acid, EDTA disodium salt and Salicylic acid, p-chloroaniline as indicator were of AR- grade. Doubly distilled water was used for preparing the different solutions. Ion-Exchange Resin: m- cresol- phenol- formaldehyde cation exchange resin was converted to hydrogen form by treating with 1.0 M hydrochloric acid for 24 hr. with intermittent changing of the acid. The exchange resin was washed several times with doubly distilled water in order to eliminate excess acid and dried in a desiccator containing anhydrous calcium chloride to remove the residual water in the beads, sieving the air dried exchanger into two different sizes (0.031 and 0.022 cm).

**Kinetic Measurements:** For kinetic measurements the modified limited batch technique was employed, because of its relative simplicity over the column and shallow-bed arrangement[4]. Known volumes (100 ml) of the ferric solutions with required percentage of isopropanol, were placed in a pyrex glass three necked flask (cap. 500 ml) and subjected to continuous mechanical stirring in a thermostated water bath ( $\pm 0.1^\circ\text{C}$ ) at the desired temperature. Weighed amounts of m- cresol- phenol- formaldehyde were then introduced into the flask, and zero time for the reaction was recorded directly after addition of the resin. Aliquots were taken out at appropriate time intervals and the sorption process was checked by immediate titration of ferric solution (1ml) using suitable method.

To evaluate the effect of isopropanol concentrations on the rate of sorption, experiments were performed for different particle sizes with different isopropanol concentrations at three different temperatures (25 , 40 and  $60 \pm 0.1^\circ\text{C}$ ).

## Results

As the limited batch technique was used, the equations developed by Boyd et. al[5] and improved by Reichenberg[6] were used. The extent of reaction (F) is expressed as:

$$F = \frac{Q_1(\text{The amount of exchange sorption at time } t)}{Q_{\infty} (\text{The amount of exchange sorption at infinite time})}$$

Three different steps can determine the rate of exchange:

(a) Particle diffusion (b) liquid films diffusion and (c) mass action.

The conditions of these experiments were set to study the particle diffusion mechanism only. As the rate-determining step is diffusion through the ion – exchanger particle, the following equation is valid:

$$F = 1 - \frac{\pi^2}{6} \sum_{n=1}^{\infty} \frac{\exp(-n^2 B)}{n^2}$$

Where  $B = \pi^2 D_i t / r^2$ ,  $r$  = radius of the particle,  $D_i$  = effective diffusion coefficient of the two ions undergoing exchange within the exchanger.

Values of  $B_t$  as a function of F may be calculated from tables reported previously by Reichenberg[6]. Plotting  $B_t$  vs. t at different temperatures given a straight line passing through the origin (Fig.1). All the plots drawn follow the least squares method. The B values are calculated from these plots and are given in table 1. The results of variation of particle size of the exchanger are presented in Fig.2 in terms of plots of  $B_t$  vs. t. These plots indicate that for large size the rate is slower. The influence of different proportions of isopropanol on the rate of sorption is indicated in Fig.3.

The energy of activation  $E_a$  has been determined by using the Arrhenius type expression.

$$D_i/D_o = \exp^{-E_a/RT}$$

from the  $D_i$  values obtained at two different temperatures.

The pre-exponential constant  $D_0$ , gives the entropy of activation ( $\Delta S^*$ ) as:

$$kT$$

Where  $k$ ,  $d$  and  $R$  are the Boltzmann, Planck and gas constants respectively,  $d$  is the average distance between the successive exchange sites and is taken as 5 Å and  $T$  is the temperature (°K). All lines have been drawn following the method of least squares.

### Discussion

The rate - determining step of the ion exchange was ascertained by noting that the exchange rate was markedly dependent on the particle size of the exchanger, the rate increased with decreasing particle size (Fig.1). This clearly indicated diffusion controlled process and is not one controlled by the chemical interaction of the exchanging ions because in the latter case the exchange rate would be independent of particle size. Distinction between particle diffusion and film diffusion was then made by the nonlinear behavior of  $\log(1 - F)$  versus  $t$  plots (Fig.2) indicating that the rate is governed neither by film diffusion nor by a mass action mechanism[7].

The shapes of these plots, called McKay plots[8] are similar to those obtained for independent radioactive decay. The curves can be resolved[9] into two linear components. This indicates two interdiffusion processes; a faster one corresponding to the residual curve and a slower one corresponding to the later linear portion of the McKay plot contributing to the overall rate of exchange. This observation is further confirmed by the shapes of  $F$  versus  $t$  plots (Fig.1), which indicate that rapid initial uptake, is followed by slower uptake of the effective ions. This suggests that the effective diffusion coefficients in the present system, is comprised of two components, which may be attributed to the simultaneous diffusion of the counter ions through the pores of different sizes and electric fields. It is also clear from the residual curves that with the rise in temperature, the contribution of the faster component of the effective diffusion is increased. These observations are similar to those of Helfferich et. al.[10], who explained the variable interdiffusion coefficients on the basis of electropotential gradient along the diffusion path.

The plot of  $B_t$  vs.  $t$  at three different temperatures are straight lines passing through the origin (Fig.3), indicating that the rate-determining step is diffusion through the particle. The  $B$  values calculated from these plots are given in table 1. It is seen from this table the diffusion coefficient for the present systems of exchange sorption increases with increase in temperature. This is in conformity with the earlier observations of temperature effect on exchange diffusion coefficient, and may be attributed to the increase in ionic mobility with temperature[11,12].

The data obtained in table 1 indicate that the sorption of Fe(III) is greatly affected by changing the dielectric constant of the medium . It is clearly seen that the values of  $D_i$  are higher for exchange in pure aqueous medium as compared with those values obtained in presence of increasing

proportions of isopropanol. Thus, the presence of isopropanol has a retarding effect on hydrated ferric ions, which alternatively leads to a retarding effect on the exchange rate that accounts for the lower value of  $D_i$ [9,12].

The negative values of the entropies of activation  $\Delta S^*$  for all the sorption systems studied have been taken as indicative of a comparatively higher degree of mobility and the lack of an orientational effect which the ingoing ion influences upon its water environment[10].

Data given in table 1 summarizes the B and  $D_i$  values as function of temperature and prove further that a particle-diffusion mechanism is the rate controlling process. These values showed also that the rate of exchange is dependent on both the temperature and the concentration of isopropanol of the exchanging medium. It is well known that the rate of sorption increases with increasing temperature, indicating that such reactions are endothermic ones.

It is seen from Fig.1 that the relative exchange rate in the initial period increases with decreasing particle size of the exchanger. This is obviously due to the increase in specific surface area, since the exchange actually takes place through the solution-solid interface. From these results it can be seen that the diffusion coefficients depend on the radius of the exchanger[10,13].

It is found (Table 1) also, that the energies of activation ( $E_a$ ) for the exchange of Fe(III) ions, using the Arrhenius equation proceed in following sequence for water isopropanol mixtures, containing 0.0% ,< 20% <50% < 80% (v/v) isopropanol respectively. This sequence in  $E_a$  values can also be understood on the basis of higher affinity of Fe(III) ions towards the exchange resin[10,14].

From the previous data we can be deduced that the values of activation energy for the exchange of ferric ions using the Arrhenius equation in pure aqueous solution are usually lower as compared with those values obtained in presence of increasing proportions of isopropanol. this may be due to the low swelling of the resin particles as a results of the decrease in the dielectric constant of the media, with addition of different proportions of isopropanol [15].

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**Table 1: Values of diffusion coefficients and energy of activation calculated for the exchange of Fe(III)/H(I) on m- cresol- phenol formaldehyde cation exchange resin.**

Isopropanol % (v/v)	Radius of particle cm	$B \times 10^{-2} (s^{-1})$			$D_i \times 10^{-6} (cm^2/s)$			$E_a$ Kcal/mole	$D_0 \times 10^{-9}$	$-\Delta S^*$ eu 40 °c
		25 °c	40 °c	60 °c	25 °c	40 °c	60 °c			
0.0	0.031	3.2	2.7	1.8	3.11	2.63	1.75	3.23	760	21.73
	0.022	3.8	3.3	2.2	1.87	1.62	1.08	3.08	496	22.58
30	0.031	2.9	2.2	1.6	2.83	2.14	1.56	3.35	590	22.30
	0.022	3.6	2.5	2.0	1.77	1.23	0.98	3.31	344	23.30
60	0.031	2.6	1.9	1.4	25.58	1.85	1.36	3.59	465	22.71
	0.022	3.2	2.4	1.7	1.57	1.18	0.83	3.56	300	23.58
80	0.031	2.5	1.8	1.3	2.44	1.75	1.27	3.78	409	22.96
	0.022	2.9	2.0	1.5	1.42	0.91	0.74	3.71	218	24.21

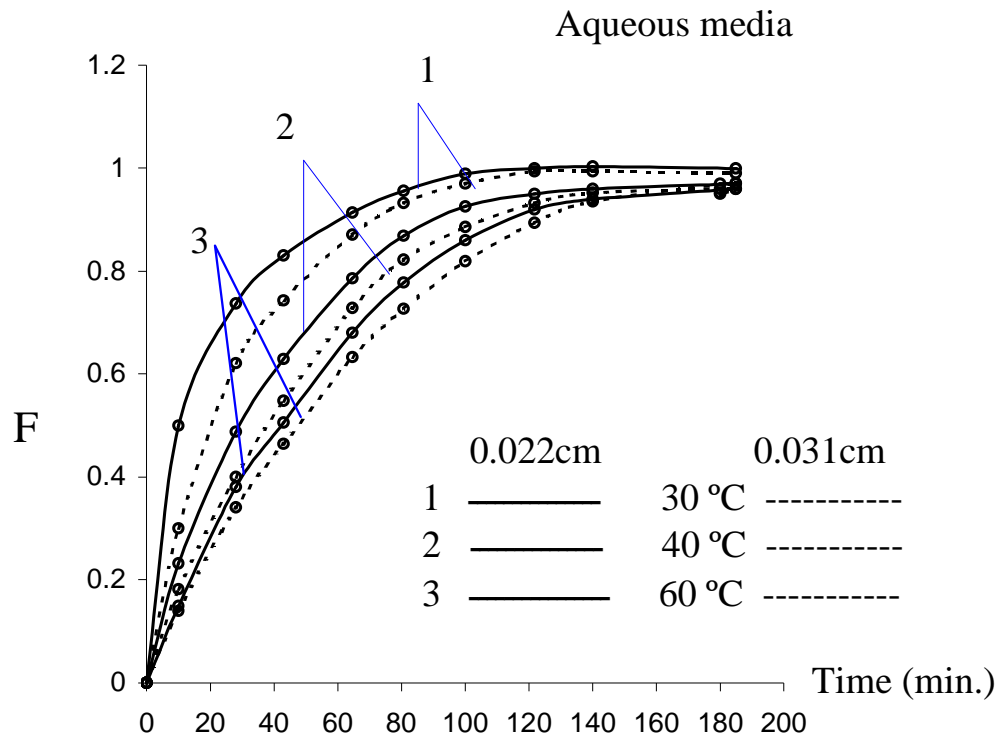


Fig.(1) Plots of F vs. time for Fe(III)/H(I) exchange.

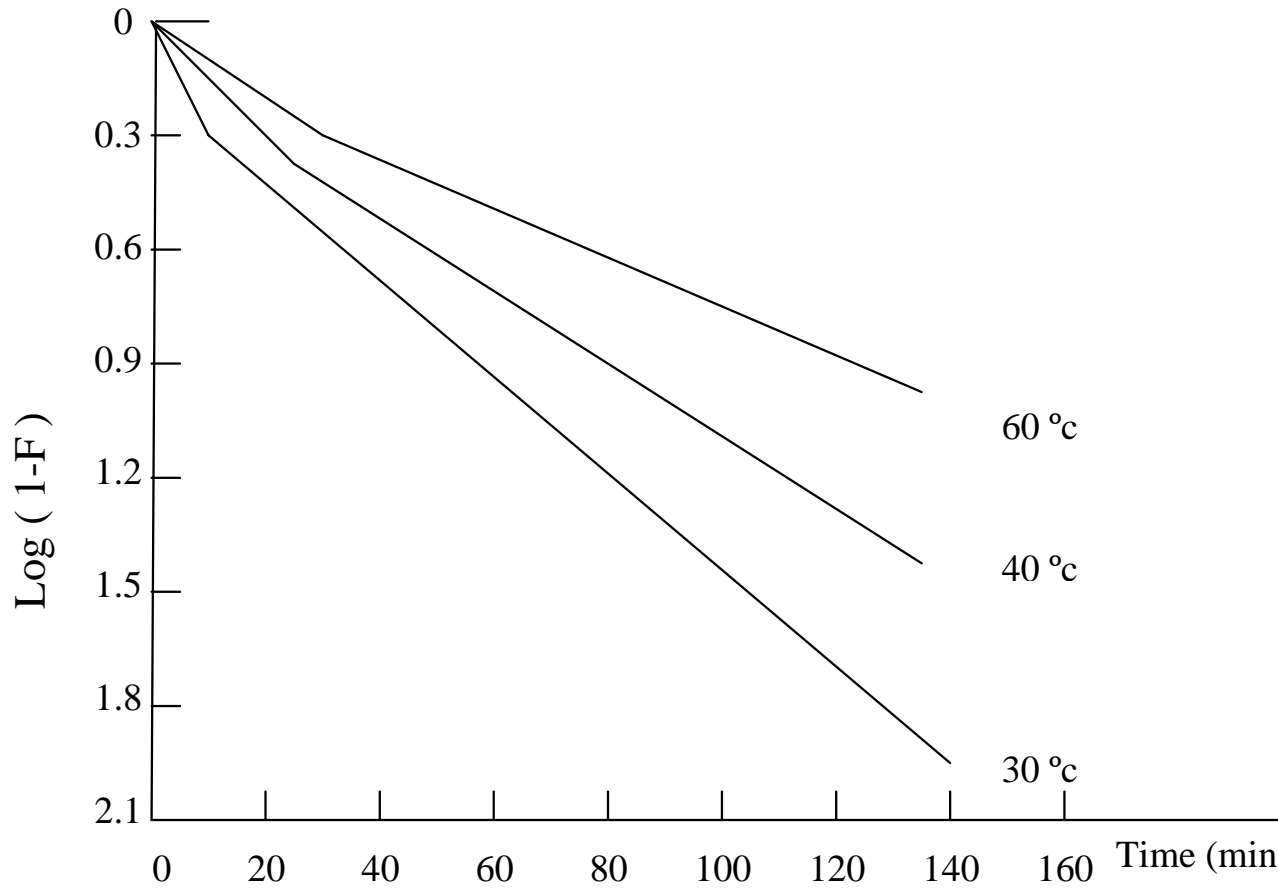


Fig.(2) Mckay plots of  $\log(1-F)$  vs.  $t$  as function of temperatures.(0.022 cm)



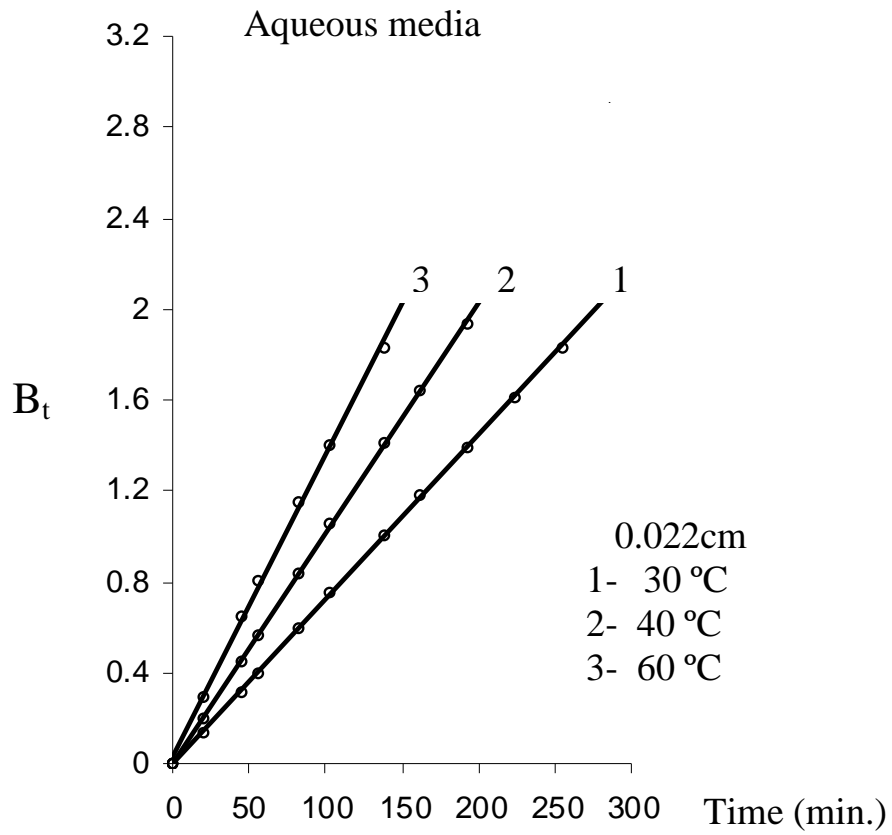


Fig.(3) Plots of  $B_t$  vs. time for Fe(III)/H(I)