

# RADIO-TRACER STUDIES OF ADSORPTION OF SULPHATE IONS ON IGNITED ALUMINA

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The study of adsorption of sulphate ions on alumina has been made in dilute solutions using S-35 as tracer. The influence of concentration, temperature and pH of the medium, on the time-growth of adsorption, has been studied. The process is seen to be rapid, giving rise to a stable adsorption phase. The energy involved in desorption has also been determined.

## INTRODUCTION

Adsorption of certain anions from dilute aqueous solutions at micro and tracer concentrations on various metal oxides has recently been reported from this laboratory (Prasad & Tripathi 1965, 1967; and Tripathi 1970). The present work was aimed with a view to study, in some detail, the adsorption of sulphate ions by ignited alumina. The choice of this adsorbent was made because of its catalytic properties and its importance (Gilmore and Newton 1967; Jacimovic *et al.* 1969; Kar 1958; and Venturello & Burdese 1951) in various surface-involved chemical processes, viz., chromatography, ion exchange, separation of some rare earths and carrier free isotopes. The present paper reports the results of the study of sulphate ion adsorption from dilute aqueous solution on alumina; S-35 being used to label the adsorbate phase.

## EXPERIMENTAL

The method consisted of keeping of weighed amount of the adsorbent in contact with the labelled adsorbate solution and determining the extent of adsorption from the corresponding decrease in the radioactivity in the solution. All the measurements were made at a constant temperature ( $30 \pm 0.1^\circ\text{C}$ ), except where the effect of temperature was to be studied and for this, separate experiments were carried out at each of the constant temperatures  $1^\circ\text{C}$ ,  $10^\circ\text{C}$ ,  $20^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $50^\circ\text{C}$ .

The experimental procedure for the measurement of adsorption and the counting technique were the same as reported earlier (Prasad & Tripathi 1965, 1967).

## MATERIALS

Extra pure alumina (Riedel, Germany) for chromatographic purposes was used for the present studies. Before use, it was treated with concentrated HCl and then washed repeatedly with hot boiling distilled water. Then, after slow drying, it was

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ignited at 450°C for 12 hours, and cooled slowly to room temperature. The powder thus obtained was finally sieved to obtain particles of size 150-175 mesh. The adsorbent sample once prepared was used throughout the work.

B.D.H. A.R. grade sodium sulphate and double distilled water were used to prepare the adsorbate solution. Solutions of required concentrations were prepared from a stock solution of 0.1 M by successive dilutions.

The carrier-free isotope viz., S-35, supplied by B.A.R.C., Trombay, Bombay, in the form of sulphuric acid in dilute HCl, was used to label the adsorbate solutions. Before use, it was, however, rendered free from the large excess of HCl, following the method of Hackerman and Stephens (1954).

#### MEASUREMENT OF pH

pH of the solutions was varied in the range 0.5—11 pH values; HCl in the acidic range and potassium carbonate in the alkaline range were used to adjust (Mehta 1963) the pH. The pH of the solution was finally measured with the help of a line operated Photovolt (model 115) pH meter, the precision of which was 0.1 pH unit.

#### RESULTS AND DISCUSSION

The general nature of the variation of adsorption of sulphate ions on alumina at constant temperature is shown graphically as plots of amount adsorbed/g. alumina against time in Fig. 1. It is seen that the adsorption is rapid in the beginning and

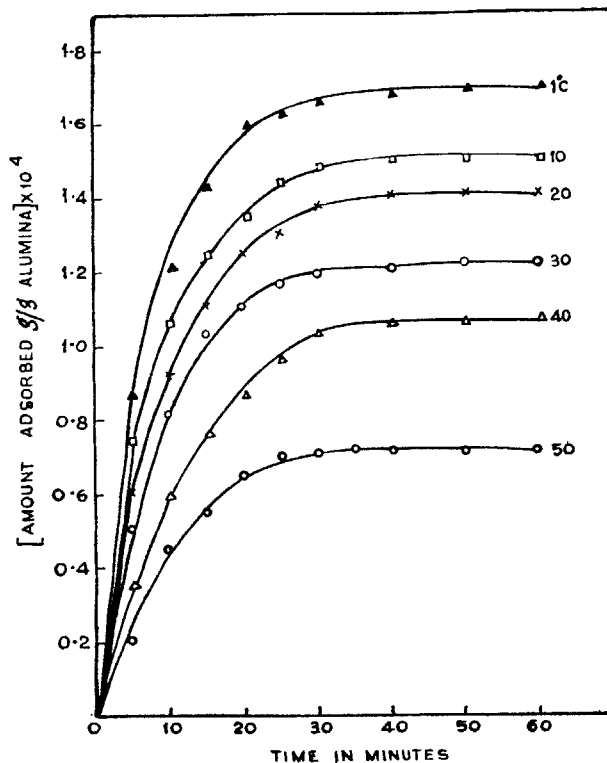


FIG. 1. Time-variation of adsorption of sulphate ions ( $10^{-3}$  M) on alumina at various temperatures

becomes slower later to reach finally a saturation. This last is attained quickly within about 30 minutes. The time-growth of adsorption is smooth and continuous upto saturation, beyond which no further change is found, despite long duration of time of contact (24 hours). This indicates that the process involved is uniform and unaccompanied by any complication. Further, it is seen to be a first order process, following the characteristic equation  $-kt = 2.303 \log (1-f)$ , where  $f$  is the fraction adsorbed at any instant. The value of specific reaction rate,  $k$  is  $0.0987 \text{ min}^{-1}$  at  $30^\circ\text{C}$ .

The dependence of adsorption on the concentration of the adsorbate was studied in the concentration range  $10^{-12} - 10^{-2} \text{ M}$  (Table I). The plot of logarithm of saturation values of adsorption against logarithm of equilibrium concentrations gives a straight line indicative of the applicability of the Freundlich isotherm; the slope,  $1/n$  is found to be 0.936, a value very near to unity. Similar are the results of Schweitzer and Bomar (1955) for the adsorption of sulphate ions by insoluble substances. For such dilute solutions, as actually used in the present investigation, a value approximating to one, for  $1/n$  is anticipated on the basis of the modifications of Langmuir's isotherm.

The study at various temperatures shows that the general nature of the time-variation of the adsorption remains sensibly unaltered (Fig. 1) though an increase in temperature influences to a great extent both the rate as well as the total amount of adsorption. It is found that the amount adsorbed at equilibrium is greater at lower temperatures, decreasing slowly to a noticeable extent with gradual rise in temperature. Thus, the amounts adsorbed at equilibrium are  $1.698 \times 10^{-4} \text{ g}$  and  $0.722 \times 10^{-4} \text{ g}$  respectively, at temperatures  $1^\circ\text{C}$  and  $50^\circ\text{C}$  (Table II). It is interesting to note that in spite of the above variation in the net amount adsorbed, the time

TABLE I  
*Variation of the amount of sulphate ions adsorbed at various concentrations*  
(Temp :  $30^\circ\text{C}$ )

Initial concentration of the adsorbate (M)	Amount of sulphate ions adsorbed on one g alumina (g)
$1.0 \times 10^{-2}$	$0.097 \times 10^{-2}$
$1.0 \times 10^{-3}$	$0.153 \times 10^{-3}$
$1.0 \times 10^{-4}$	$0.122 \times 10^{-4}$
$1.0 \times 10^{-5}$	$0.240 \times 10^{-5}$
$1.0 \times 10^{-6}$	$0.432 \times 10^{-6}$
$1.0 \times 10^{-7}$	$0.532 \times 10^{-7}$
$1.0 \times 10^{-8}$	$0.572 \times 10^{-8}$
$1.0 \times 10^{-9}$	$0.215 \times 10^{-9}$
$1.0 \times 10^{-10}$	$0.395 \times 10^{-10}$
$1.0 \times 10^{-11}$	$0.436 \times 10^{-11}$
$1.0 \times 10^{-12}$	$0.124 \times 10^{-12}$

required to attain saturation is not affected to any large extent as a result of the corresponding variation in the temperature.

The detachment of the adsorbed ions was studied in three different series of experiments, (i) release of ad-ions to water, (ii) exchange of adsorbed ions with identical but un-labelled sulphate ions in the solution and (iii) removal of ad-ions as a result of heating the adsorbed sample at elevated temperatures. The results (Table III) show that the desorption of sulphate ions is far slower than the process of adsorption and that the ions once adsorbed on the surface show great reluctance towards detachment. Thus, the release of ad-ions to water at 30°C is only 25.73 per cent; the exchange with the unlabelled identical ions is still slower, being only 12.72 per cent. It is further seen that the release of ad-ions to water is dependent upon temperature, the percentage desorption increasing with increase in temperature (Table III). Heating the adsorbed sample at elevated temperatures shows a diminution in radioactivity; the extent is dependent upon temperature (varied over 150°C—

TABLE II  
*Adsorption of sulphate ions on alumina : variation with temperature*  
(Adsorbate concentration :  $1 \times 10^{-3}M$ )

Temp. °C	1	10	20	30	40	50
Amount adsorbed by one gram adsorbent ( $g \times 10^4$ )	1.698	1.515	1.420	1.220	1.072	0.722

TABLE III  
*Desorption of sulphate ions adsorbed on alumina*  
A—Release of ad-ions to water and exchange with unlabelled ions

% release of adsorbed ions to water after 2 hours					% exchange of ad-ions with unlabelled adsorbate solution at 30°C
Temperature °C					
20	30	40	50	60	
18.11	25.73	37.22	42.90	49.17	12.72

B—Per cent Detachment by heating the adsorbed sample at higher temperatures

Temp. °C	Duration of heating (hrs.)			
	1	2	4	6
150	0.31	0.69	0.99	1.25
200	0.57	0.95	1.73	3.81
250	1.68	3.97	9.88	14.06
300	4.55	8.72	15.31	28.17
350	10.09	13.89	24.82	39.56
450	19.48	24.72	46.15	70.12

450°C) and also upon the duration of heating. The results show that the detachment is slower in the temperature range 150°C—250°C, and is greatly accelerated at higher temperature (300°C—450°C). From these results it is evident that the removal is not completed entirely even in 6 hours of heating and at an elevated temperature of 450°C. This result is indicative of a stronger binding between the ions and the alumina surface, as distinct from the simple and completely reversible physical adsorption. The energy requirements for such a process should be high. This deduction has actually been confirmed (*vide infra*).

The time-rate study of the desorption of ad-ions from the alumina surface indicates that the desorption is also a first order process. The energy of activation for desorption, obtained from the slope of the usual straight line plot of  $\log k$  against  $1/T$ , is found to be 10.2 kcal. deg<sup>-1</sup> mole<sup>-1</sup>. Thus the forward process though appearing to be non-activated, the reverse one involves significant energy of activation.

The results for the adsorption of sulphate ions on alumina at different values of pH indicate that the general nature of the time-growth of adsorption remains essentially similar though the rate as well as the total amount adsorbed are different at different pH values. It is further observed that adsorption increases initially in the highly acidic solutions upto a maximum (pH = 4.2), and thereafter with further increase in pH it decreases continuously (Fig. 2; reproduced from earlier publication Tripathi & Prasad 1970). It is thus evident that the adsorption of sulphate ions on alumina is favoured in the acidic region of the pH scale.

The rapid adsorption of sulphate ions by alumina and greatly favoured at lower temperatures is indicative of a fast process very similar to that of a simple physical adsorption. Use of the ions and activated alumina surface, should involve low activation energies even if some sort of quasi-chemical interaction takes place. This supposition finds support from the large resistance towards detachment of the ions once adsorbed on the alumina surface, making the adsorbed phase very stable, quite distinct from that of a readily reversible physical adsorption. It appears that as a consequence of superimposition of comparatively stronger coulombic interactions, the physically adsorbed species are converted to the final stable adsorption phase.

Adsorption of ions from solutions by solids is modified largely due to the electrical forces resulting from the prior presence of charged particles on the surface itself or/and in its immediate vicinity. It becomes significantly important when a variation in hydrogen ion concentration is considered particularly in case of adsorption on surface prone to interactions with H<sup>+</sup> and OH<sup>-</sup> ions. The surface of alumina in contact with water is covered with a hydroxide layer, which ionises as an acid or a base, depending upon the circumstance (O'Connor *et al.* 1956). The surface properties of alumina, studied by streaming potential and micro-electrophoretic methods (Johansen & Buchanan 1957 a, b), have thus been explained in terms of ion adsorption and ion-exchange. Such a consideration indicates that near the surface of alumina (having a positive charge in low pH region) accumulation of anions (chloride and hydroxyl ions, in addition to the adsorbate sulphate ions) occurs in the Stern plane and the 'diffuse layer'. As the magnitude of the  $\xi$ -potential and the thickness of the double layer depend on the above accumulation, a change in the concentration of these ions will influence to such an extent as to reverse the sign of zeta potential in the extreme case. This happens due to the neutralisation

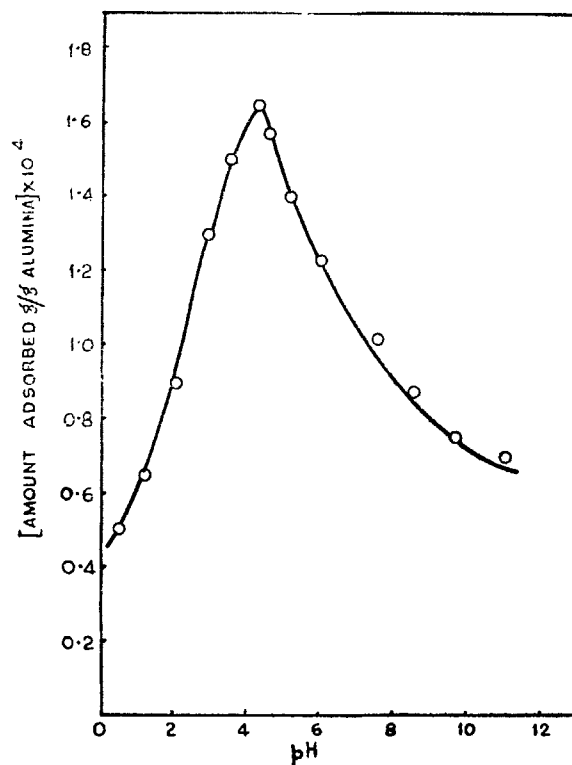


FIG. 2. Variation of adsorption amount with pH of the medium at 30°C (Tripathi & Prasad 1970)

of the charge or/and diminution of the thickness of the double layer to such an extent that it eventually collapses and re-forms with the charge reversed. It is at this stage of zero charge that the measured adsorption represents the true adsorption, uninfluenced by electrical field. With an increase in the pH of the medium, the  $\text{OH}^-$  ion concentration increases (though that of sulphate ions remains constant) resulting ultimately, in an overall increase in the concentration of the counter ions. Thus, with further rise in pH, the above characteristic stage is reached when the formation of the double layer with opposite sign sets in. The adsorption of sulphate ions which is large before this pH value should decrease. The present results are in close conformity with this deduction.

The above deduction finds support from the findings of Modi and Fuerstenau (1957, 1960) on the streaming potential studies of corundum in aqueous solution. They have concluded that at low pH values, near 4.0, there is an excess of positive charge on the alumina surface. On the basis of this positive charge, the increasing adsorption in the low pH range and the peak in the adsorption-pH plot (Fig. 2) are satisfactorily explained in much the same way as described above. Beyond the peak at pH 4.2, the adsorption is found to decrease and at still higher pH values, the alumina surface becomes oppositely charged, leading ultimately to a decrease in the net adsorption due to the repelling effect.

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