

Effect of Alum and pH on the Adsorption of Cationic Polyacrylamide onto Cellulose Fibres*

DULESWAR MAHANTA

ABSTRACT

The adsorption of two high-molecular weight and one low-molecular weight quaternized cationic polyacrylamide (QCPAM) onto bamboo bleached kraft pulp was studied in presence of three different addition levels of alum. The effect of pH on the adsorption of QCPAM as well as of alum onto the pulp was also investigated. It was observed that adsorption of aluminium increased as the pH of the medium was raised. The adsorption of the polymer increased with increased concentration of alum in neutral or alkaline medium. It is suggested, therefore, that some correlation between precipitated alum on the surface of the fibres and QCPAM adsorption must exist.

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INTRODUCTION

Various factors affect the adsorption of cationic polyacrylamide onto cellulose substrate, of which, the effects of simple electrolytes exhibit considerable variations. That simple electrolytes vary in their effect on the adsorption of cationic polyacrylamide onto cellulose substrates is evident from the published literature^{1,2}. Both basic and acidic radicals of the electrolyte play important roles in this regard. The mode of action of the electrolytes on adsorption depends not only on the concentration of the electrolytes but also on the concentration of the polymer used^{1,2}.

In an earlier communication, Mahanta *et al*³ have shown the effects of some parameters such as (i) molecular weight and charge density of the polymer (ii) pH of the reaction medium (iii) mechanical action on the pulp fibres and (iv) added concentration of foreign electrolytes on the adsorption of quaternized cationic polyacrylamide (QCPAM) onto bamboo bleached kraft pulp. It was reported in that communication that the adsorption of QCPAM onto cellulose upon increased

addition of alum, after an initial drop in adsorption, tended to increase. Addition of alum (0.25 to 2.5 molar) and QCPAM (10 mg.g⁻¹) in the earlier publication was higher than that actually used in paper making systems. This study, therefore, includes the adsorption of QCPAM onto pulp from dilute solutions of QCPAM in the presence of different alum concentrations.

It is reported that, in alum solutions, species of various electric charge develop, depending on the pH of the medium^{9,10}. Adsorption of QCPAM onto pulp fibres is mainly by charge interaction³. Its adsorption, therefore, will be affected both by concentration of alum and by pH. Adsorption of QCPAM onto pulp fibres as a function of pH with and without the presence of alum onto the pulp fibres at various pH levels were studied and the results are reported in this article.

Regional Research Laboratory, Jorhat-785006
Assam (India).

EXPERIMENTAL

A MATERIALS :

The cationic polymers (QCPAM), used in this investigation were prepared in the laboratory by Mannich reaction of non-ionic polyacrylamides also prepared in the laboratory. The method of polymerization and the subsequent conversion of the non-ionic polymer to the cationic one are reported in earlier publications^{3,4,5}.

The characteristics of the polymers used in this investigation are shown in Table-I.

TABLE-I
CHARACTERISTICS OF THE CATIONIC
QUATERNARY POLYACRYLAMIDE USED
FOR ADSORPTION

Polymer No.	Intrinsic viscosity (Cm ³ g ⁻¹)	Molecular weight x 10 ⁻⁵ (g mole ⁻¹)	Charge density (m eq g ⁻¹) ^c
1	60	0.94 ^a	1.2
2	370	9.12 ^a , 7.9 ^b	2.22
3	400	10.1 ^a	1.8
4	1740	63.2 ^a (58.3) ^b	4.86

a. Mol. Wt determined by using the formula,

$$M_w = \left[\frac{[\eta]}{6.31 \times 10^{-3}} \right]^{1.25}$$

ref. Scholtan, W. *Makromol Chem.* **14**, 169, (1954)

b. Mol. Wt determined by light scattering.

c. Charge density was determined by colloid titration using potassium polyvinylalcohol sulphate (PVSK) solution which dissociates completely above pH 2 and whose charge can be taken as 6.17 m. eq g⁻¹ of polyanion.

Before use in adsorption experiments, the QCPAM polymers were purified by dialysis for about 10 days and then dried under vacuum at 30°C.

The pulp used in this investigation was a bleached kraft bamboo pulp. The method of preparation of the pulp and its evaluation are described in an earlier publication⁴. Since the pulps were to be used as the adsorbents, it was necessary to remove as many foreign ions as possible alongwith any other material which

might have interfered with the adsorption of the polyacrylamides. In order to remove the ash content of the pulp, the pulp was soaked in 0.1 N HCl at room temperature (23°C) followed by thorough washing with deionized distilled water. The fines fraction of the pulp was removed by screening the pulp over a 100 mesh stainless steel screen. The chemical analysis of the screened pulp showed: Alpha cellulose 85.48%, ash 0.03%, lignin 1.96%, pentosans 8.8%, carboxyl group 0.682%, methoxyl 0.91%.

Water used in this investigation was first passed through an ion-exchange resin and subsequently distilled in a glass distillation apparatus. The water was collected in a glass reservoir and all the experiments were performed with the water from the reservoir.

The chemicals used in this investigation were all of a analytical grade and used without further purification.

B. METHODS :

Portions (1g) of the air dried pulp and enough deionized distilled water were placed in graduated measuring cylinders (250 ml capacity) equipped with ground glass stopper and shaken vigorously to break down the pulp. The cylinders were then kept in a constant temperature bath at 30°C for about 24 hrs with constant stirring to allow them to attain equilibrium with respect to cellulose swelling degree and water content.

1g of the purified QCPAM was placed in a volumetric flask (1 L capacity) equipped with a ground glass stopper. The polymer was dissolved by adding small amounts of deionized distilled water with constant shaking. When the polymer was completely dissolved the volume of the flask was made upto the mark so that the concentration of the polymer solution was 1 g (dm)³.

The adsorption experiment were performed in two series.

SERIES I :

To the measuring cylinders containing the pulp, measured volumes of alum solution were added and the flasks shaken thoroughly. 10 cm³ portions of the polymer solution (equivalent to 10 mg dry polymer) were then added to the cylinders. The cylinders were

thoroughly shaken and volume was made upto 100 cm³. The system was then kept at 30°C for 24 hrs with constant shaking. The pH of the system was brought to the desired level by adding 0.1 N Na OH or 0.1 N HCl.

SERIES 2 :

For this series of experiments, 10 cm³ of the polymer solution used in series 1 was diluted to 100 cm³ with deionized distilled water in a volumetric flask so that the polymer concentration was 0.1 g/(dm)³.

To the cylinders containing the pulp, measured volumes of alum solution were added and the flasks shaken gently. 5cm³ portions of the diluted polymer solution (equivalent to 0.5 mg dry polymer) were then added to the cylinders. The final volume in each cylinder was made upto 100 cm³. The cylinders were kept at 30°C for 24 hours with constant shaking. The pH was controlled by adding 0.1 N NaOH or 0.1 N HCl.

The pulp was then filtered through a glass funnel under vacuum. The nitrogen content of the fibre was determined by micro Kjeldahl method. Blanks were also run simultaneously using untreated pulp. The difference in nitrogen content was taken as the nitrogen of adsorbed polymer. The amount adsorbed was then calculated from a calibration curve.

Adsorption of aluminium onto the pulp was determined by transferring 10 cm³ of the filtrate to an Erlenmeyer flask and the pH adjusted to 9.5 by adding NaOH solution. 10 cm³ of the buffer solution of pH 9.0 (103.5 g NH₄Cl mixed with 133 cm³ concentrated NH₄OH and then diluted to 1000 cm³ with distilled water) and 10 cm³ 8-hydroxyquinoline in chloroform were added to the filtrate and then transferred to a separating funnel. The aluminium - 8 - hydroxyquinoline chelate was then extracted with chloroform and the absorbance of the extract determined in a spectrophotometer at 390 nm. The concentration of aluminium in the solution before adsorption was also determined in the same way. The difference in concentration before and after adsorption gave the amount of aluminium adsorbed.

RESULTS AND DISCUSSION.

That alum behaves in a different manner from other simple electrolytes in retarding the adsorption of

cationic polyacrylamide onto a bamboo bleached kraft pulp is shown in our earlier communication³. It has been shown there that above certain alum concentrations (>0.1 M) the adsorption of QCPAM onto pulp increases with increasing alum concentration. The reasons suggested for this abnormal behaviour of alum in adsorption of QCPAM onto bamboo bleached kraft pulp were that a small concentration of alum was sufficient to compress the electrical double layer whereby the attraction between the sulphate ion and the electrostatic field surrounding the QCPAM was high enough to encourage counter ion condensation which might help the polymer to coil up and as such the adsorption increased with increased concentration of alum.

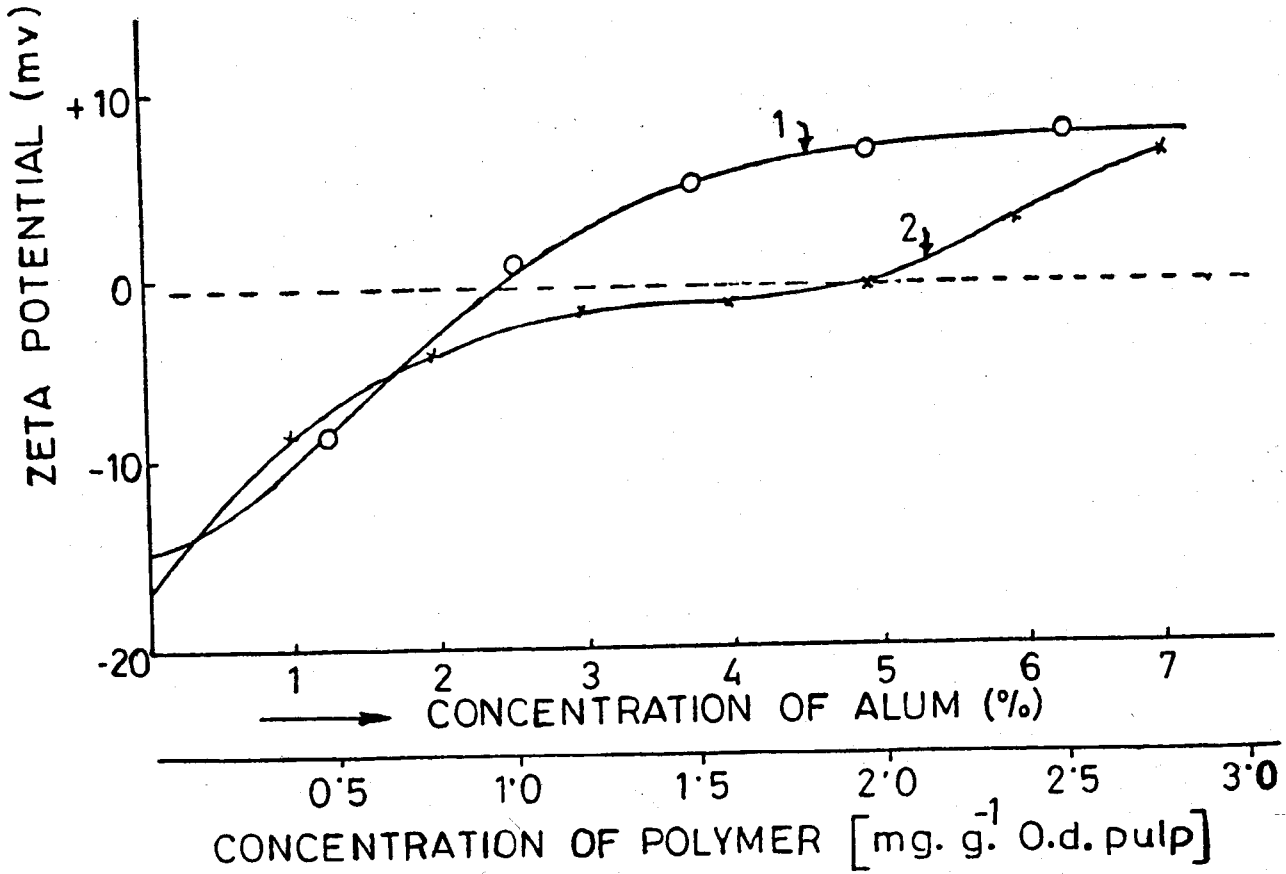
Recently, Crow et al^{6,7} have shown that the adsorption of cationic polyacrylamide onto cellulose in presence of aluminium salts is dependent upon concentration, counter ion, PH and time. These authors detected two distinct pH regions (above and below pH_p, "the precipitation pH") where the effect of alum concentration on the adsorption of cationic polyelectrolyte onto cellulose differed greatly. Below pH_p, the adsorption decreases continuously with increasing alum concentration, but above pH_p, an increase in alum concentration above 2.5×10^{-4} M significantly increases polymer adsorption once sufficient precipitate has formed.

Moore⁸ also found that increasing the alum concentration in a pulp suspension treated with a highly cationic polyacrylamide at pH 4.5-5.0, increased the drainage rate. Improvement in drainage due to a drainage aid results from its increased adsorption onto the substrate. Therefore, these findings, have some resemblance to our finding of increased adsorption of QCPAM by bamboo bleached kraft pulp after an initial decrease in adsorption of the polymer.

The zeta potential of the pulp used for the present study was -15 mV as determined by a Zetameter (Type GT-2). The Zeta potential of the pulp could be brought to zero by adding 1 mg of the polymer (polymer No. 3 Table 1) per gm of o. d. pulp or by adding 5% alum (Fig. 1).

Fig. 2 shows that adsorption of aluminium onto pulp fibers increases as the pH of the medium is increased. Thus at pH 4, the adsorption of aluminium was approximately 0.5 mg g⁻¹ of the o.d. pulp when the

FIG. 1. ZETA POTENTIAL OF THE FIBRES AS FUNCTION OF ADDITION OF (1) CATIONIC POLYACRYLAMIDE (2) $Al_2(SO_4)_3$



concentration of alum as maintained at 0.1 M. The adsorption jumped to 5 and 6 mg g⁻¹ when the pH of the medium was raised to 6 and 9 respectively, the level of alum concentration remaining constant. The same trend of adsorption was also observed by lowering the alum concentration to 0.01 M and 0.001 M. Similar observations were made by other workers in this field^{7,9}.

Graphs A, B and C in Fig. 3 representing addition level of QCPAM (Polymer No. 1 Table 1) at 10 mg g⁻¹ show that adsorption of QCPAM onto pulp increases as the pH of the medium is increased. The dotted line (Fig. 3) indicates the adsorption of QCPAM in absence of alum. It can be seen that as the pH increases, the adsorption reaches a plateau. This increase in adsorption can be explained by assuming increased ionization of the carboxyl groups of the pulp fibres as the alkalinity of the medium increases³.

FIG. 2 EFFECT OF PH ON THE ADSORPTION OF ALUMINIUM ONTO PULP FIBRES.

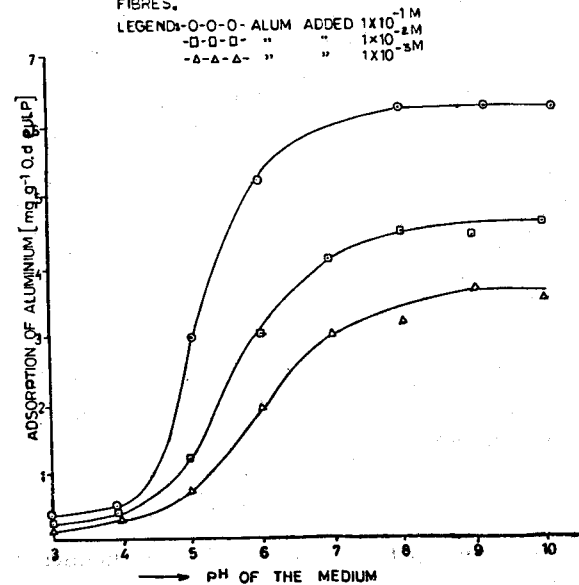


FIG 3 EFFECT OF PH ON THE ADSORPTION OF CATIONIC POLYACRYLAMIDE ONTO BAMBOO BLEACHED KRAFT PULP IN PRESENCE OF $Al_2(SO_4)_3$

LEGEND :- ALUM CONCENTRATION FOR GRAPHS A & A₁ 1×10^{-3} MOLAR
 " " " " B & B₁ 1×10^{-2} MOLAR
 " " " " C & C₁ 1×10^{-1} MOLAR
 POLYMER APPLIED FOR GRAPHS A, B & C 10 mg.g^{-1} o.d. PULP
 " " " " A₁ B₁ & C₁ 0.5 mg.g^{-1} o.d. PULP

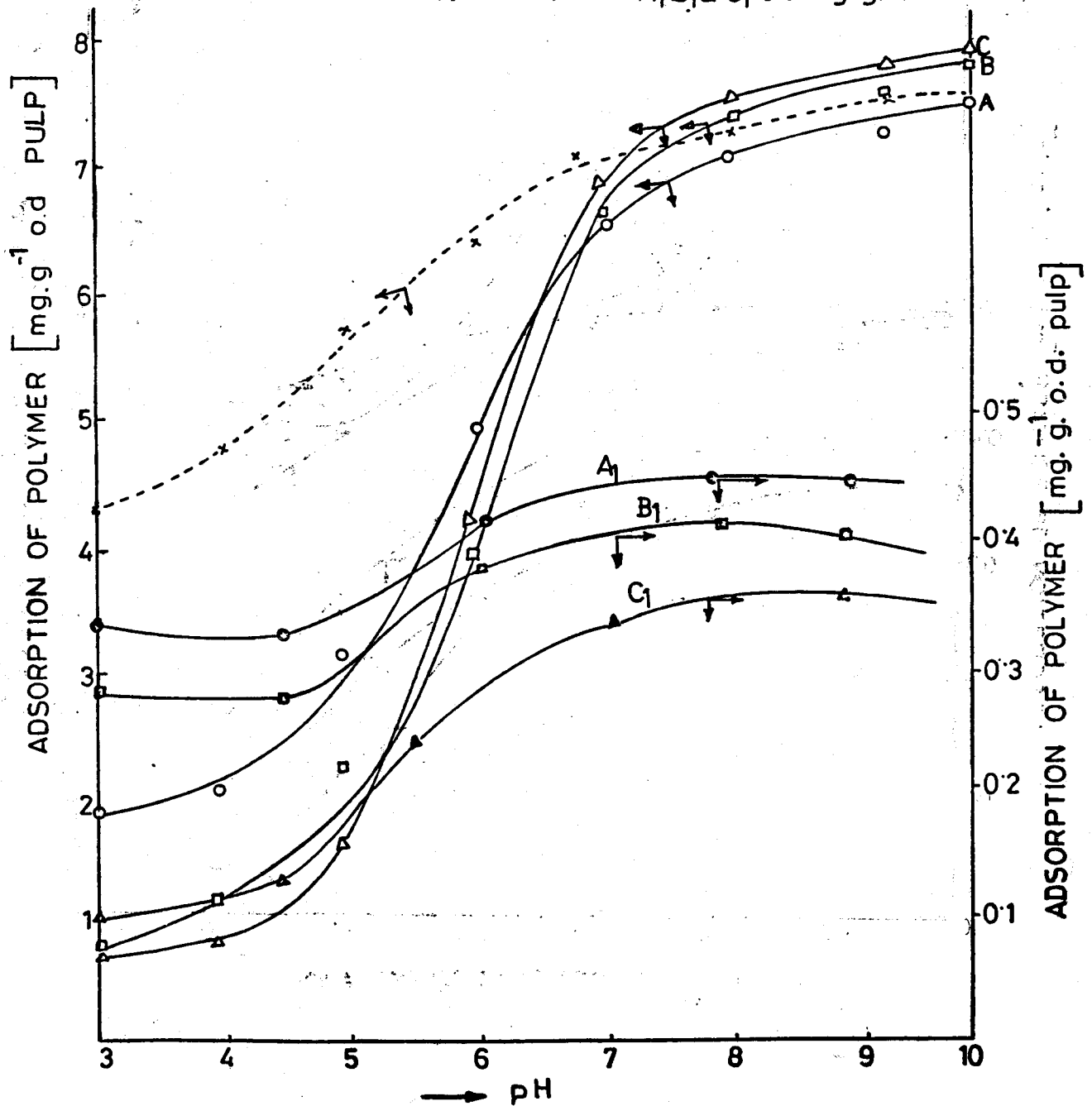
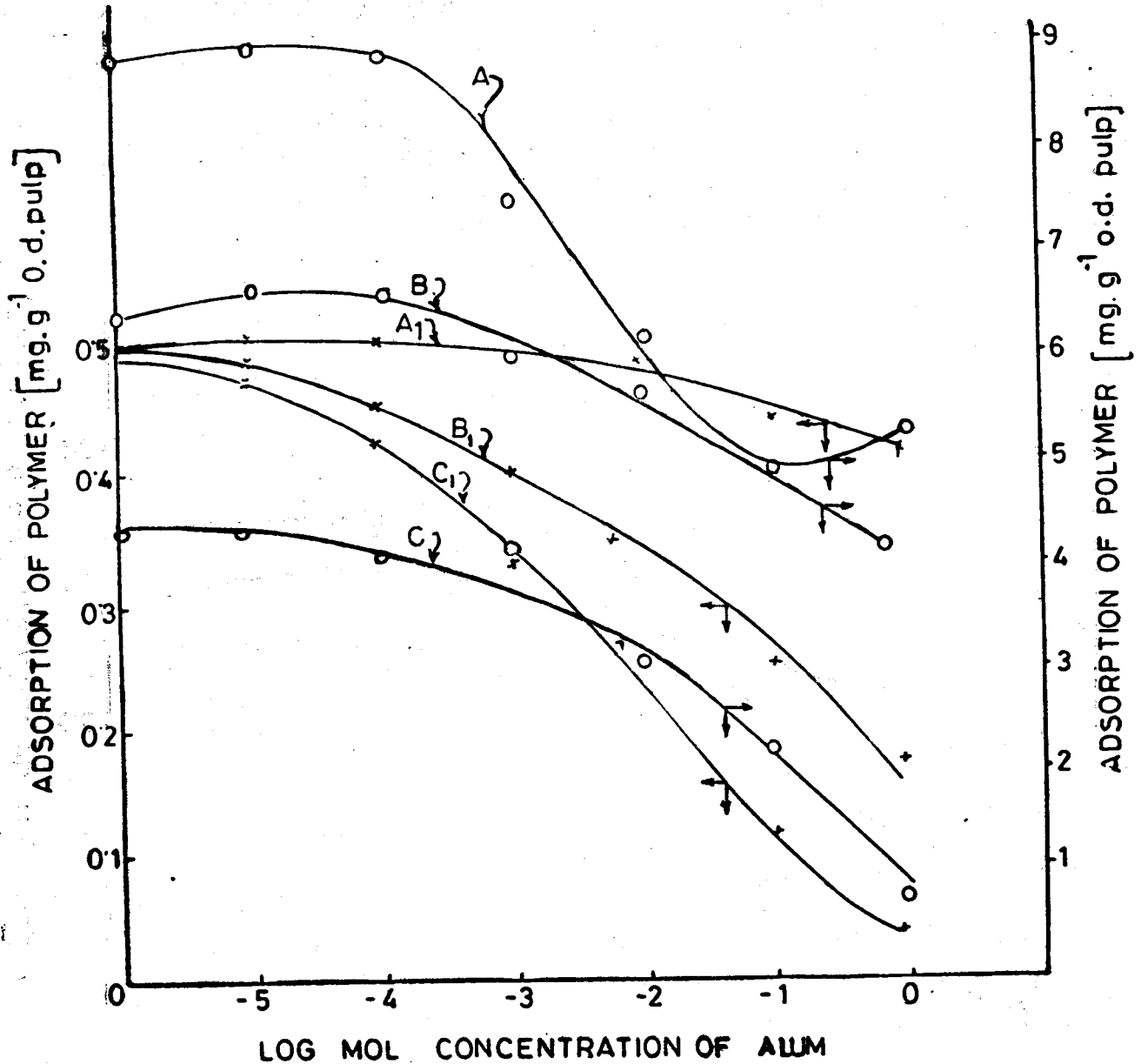


FIG 4 EFFECT OF ALUM CONCENTRATION ON THE ADSORPTION OF CATIONIC POLYACRYLAMIDE ONTO BAMBOO BLEACHED KRAFT PULP PH 4.5

LEGEND: GRAPH A & A₁ POLYMER NO 1 OF TABLE 1
 GRAPH B & B₁ " NO 2 " " "
 GRAPH C & C₁ " NO 4 " " "

POLYMER APPLIED FOR GRAPHS A, B & C → 10 mg.g⁻¹ 0.d. PULP
 A₁ B₁ & C₁ → 0.5 mg.g⁻¹ 0.d. PULP



In presence of alum (Graphs A, B and C, Fig. 3) the adsorption was low at low pH. The adsorption increased rapidly as the pH of the medium reached 5 and the trend continued till it reached an alkaline pH when the rise in adsorption became more gradual. In the region of alkaline pH, it was observed that at the same pH the adsorption of the polymer onto pulp increased with increase in alum concentration. Thus at pH 3 in presence of 0.1, 0.01 and 0.001 M alum, the levels of adsorbed QCPAM (polymer No. 1, Table-I) were approximately 0.7, 0.8 and 1.8 mg. g⁻¹; at pH 7 they were approximately 6.9, 6.6 and 6.4 mg.g⁻¹ and at pH9 they were 7.75, 7.6 and 7.25 mg g⁻¹ respectively, indicating that increased alum concentration increased QCPAM adsorption at neutral and alkaline medium.

Graphs A₁, B₁ and C₁ in Fig. 3 representing level of addition of QCPAM (Polymer No. 1, Table I) at 0.5 mg g⁻¹ also show that with increase in pH the adsorption of QCPAM onto pulp increases. At the same pH (acidic or alkaline) the adsorption of QCPAM onto pulp fibres decreases with increased concentration of alum.

Graphs A, B and C, representing addition level of QCPAM at 10 mg.g⁻¹ (Fig. 4) show the effect of alum concentration of the adsorption of QCPAM of differing molecular weight and charge density. Graph A shows the adsorption of a low molecular weight QCPAM (polymer No. 1, Table I). It is observed that above 0.1 M alum concentration this QCPAM showed a tendency to increase in adsorption. But the same polymer when the level of addition was 0.5 mg g⁻¹. (Graph A₁, Fig. 4) did not show the same trend. This is consistent with the findings of Hendrickson *et al*¹¹ who reported that percol 292, at an addition level of 0.5 mg. g⁻¹ did not increase with increasing alum concentration. Graph B, B₁, and C, C₁ of Fig. 4 represent QCPAM, polymer Nos. 2 & 4 respectively of table I) which did not show any increase even at an addition level of 10 mg per gm of o.d. pulp.

The present studies indicate that adsorption of aluminium onto cellulose fibre depends upon the concentration of alum as well as on the pH of the medium.

It is found that adsorption increased when both these parameters are raised.

The increase in adsorption of QCPAM with change in pH of the medium from acidic to alkaline, suggests that there should exist some correlation between alum precipitation and QCPAM adsorption.

The increased adsorption of QCPAM in neutral or alkaline medium with increased concentration of alum suggests that within certain limits, QCPAM is adsorbed onto the precipitated alum on the surface of the fibre.

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