

Novel biodegradable flocculants based on polysaccharides

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The waste water and industrial effluent-treatment requires both inorganic and organic flocculants. Among the organic type, polymeric flocculants (synthetic as well as natural) are preferred because of their low dosage, easy handling, inertness to pH changes, production of large cohesive flocs and versatile tailorability. The concern for environmental and ecological issues warrants the use of the biodegradable flocculant in waste water and industrial effluent treatments. Natural polysaccharides such as starch, gums, glues, alginate, etc. function as bridging flocculants. This could be accounted for by the purification and chemical modification. It has been established that by grafting polyacrylamide branches on polysaccharides, the dangling grafted chains have easy approachability to the contaminants. Among the grafted guar gum, xanthan gum, carboxy methyl cellulose and starch, grafted starch flocculates better. Starch consists of amylose (a low molecular weight linear polymer) and amylopectin (a high molecular weight, branched polymer). The grafted amylopectin is found to be a suitable flocculant for various kinds of industrial effluents. Here we summarize the various investigations carried out using flocculants based on polysaccharides.

FLOCCULATION is an essential phenomenon in domestic/industrial waste water treatment and mineral beneficiation¹⁻³. It is caused by the addition of minute quantity of chemicals known as 'flocculants'. Both inorganic and organic flocculants are used in a number of studies. Among the inorganic flocculants, the salts of multivalent metals like aluminium and iron are mostly used. The organic flocculants are essentially polymeric in nature. Both synthetic and natural water-soluble polymers are used as flocculants. Some of the important examples of synthetic polymers are polyacrylamide, poly(acrylic acid), poly(styrenic sulphonic acid), poly(diallyl dimethyl ammonium chloride) (DADMAC), etc. Among natural polymers, guar gum, starch and alginic acid are very often used as flocculants and retention aids. The synthetic flocculants are available in all the three forms, i.e. cationic, anionic and nonionic.

The extensive use of polymers as flocculants is due to their distinct characteristic attributes⁴. The polymers are convenient to use and do not affect the pH of the medium. They are used in minute quantities (1–5 ppm) and flocs formed during flocculation are larger, stronger and better settling than do the simple coagulating electrolytes. The flocculating efficiency of polymers increases with increasing molecular weight. Large tonnage use of inorganic compounds produces a lot of sludge, which is hardly a problem in case of polymeric flocculants. Among polymeric flocculants, the synthetic polymers can be tailor made by controlling the molecular weight, molecular weight distribution, chemical structure of polymers, nature and ratio of functional groups on polymeric backbone. Thus due to versatile tailorability, synthetic polymers are very efficient flocculants. However, they are not shear resistant. Natural polymers mainly polysaccharides are fairly shear stable, biodegradable and easily available from reproducible farm or forest resources. The biodegradability of natural polymers reduces their shelf life and needs to be suitably controlled. Their required dosage is large and their solutions and flocs lose stability and strength respectively due to biodegradability. It is thus evident that all polymers whether natural or synthetic have one or other disadvantage. In the past, several attempts have been made to combine the best properties of both by

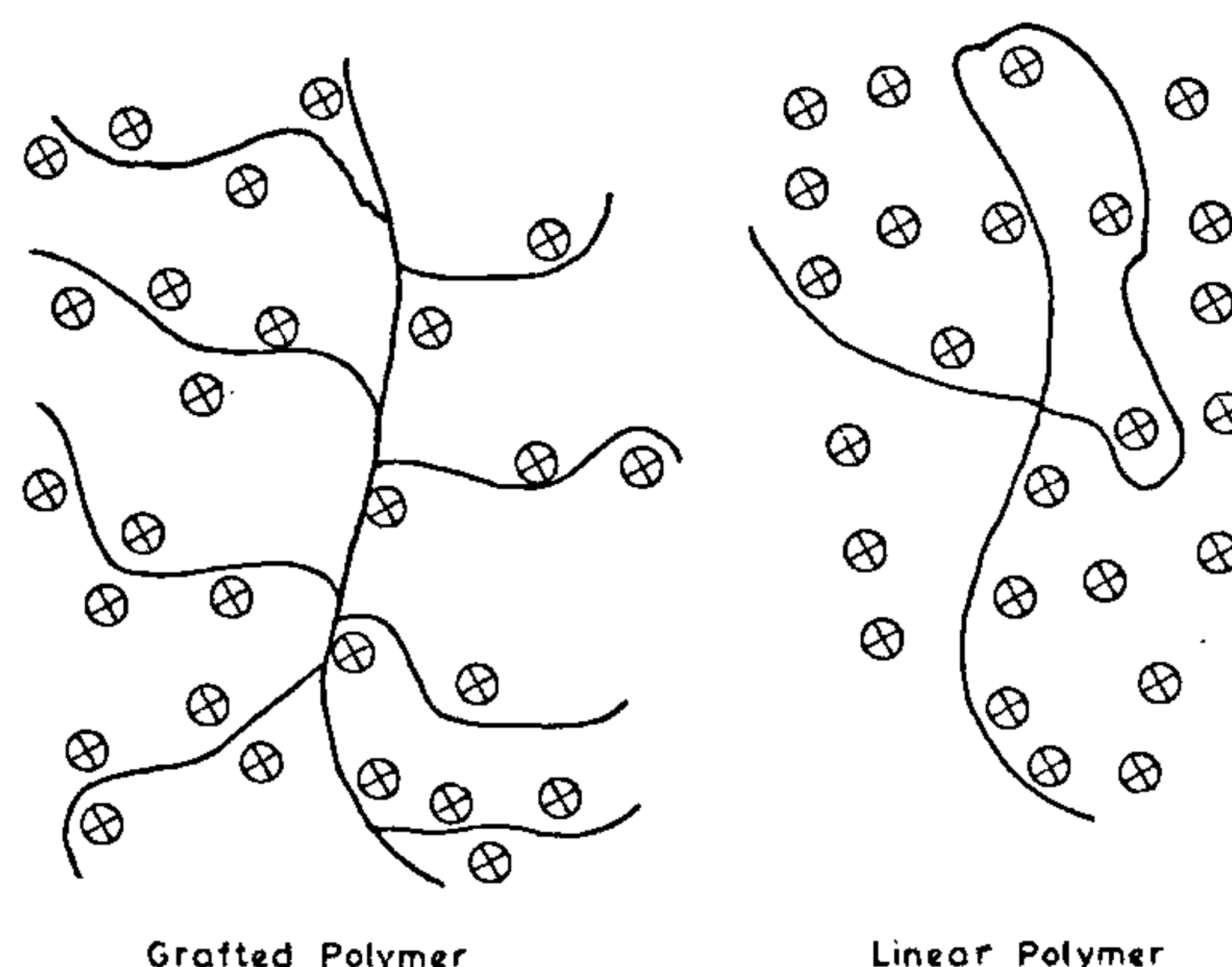


Figure 1. Approachability of grafted and linear polymers to the contaminants in an effluent.

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grafting synthetic polymers onto the backbone of natural polymers after purification^{5,6}. One of the great advantages thus gained is the consequent reduced biodegradability because of the drastic change in the original regular structure of the natural polymer as well as the increased synthetic polymer content within the product. It is also observed that grafting of shear degradable polymers onto rigid polysaccharide backbone provides fairly shear stable systems^{6,7}.

It was envisaged⁶ that by grafting flexible polyacrylamide chains on polysaccharides such as guar gum, xanthan gum, carboxy-methyl cellulose and starch, it is possible to develop efficient, shear stable and biodegradable flocculants for treatment of industrial effluents and mineral processing. In these flocculants, the flexible chains of polyacrylamide are grafted onto rigid backbone of polysaccharides. Hence, the approachability of polyacrylamide chains for metallic and non-metallic contaminants increases significantly⁶ (Figure 1). Thus they are endowed with highly efficient attributes.

Surface charges are generated on the solid particles in a suspension by three ways⁸. One is the isomorphous substitution in the solid lattice. The second is the ionization of surface groups (such as an -OH group in mineral oxides, carboxyl groups for latex particles and carboxyl or amino groups for proteins). The third method is the preferential adsorption of ions or ionisable species from the suspending medium. Because of this surface charge, ions of

opposite charge in the solution will be attracted towards the surface. There will be a higher concentration of counter ions close to the surface, than in the bulk of the liquid. This concentration falls off with increasing distance from the particle surface. Thus, there is a bound layer (Stern layer) of counter ions at the particle surface and after this layer, a more diffuse layer still exists. Only the bound layer moves with the particles. So there is a plane of shear between the bound layer and the diffuse layer. The potential difference between the plane of shear and the bulk solution is called the 'zeta potential'. These phenomena give rise to the electrical double layer which surrounds the colloidal particles. The double layer composed of

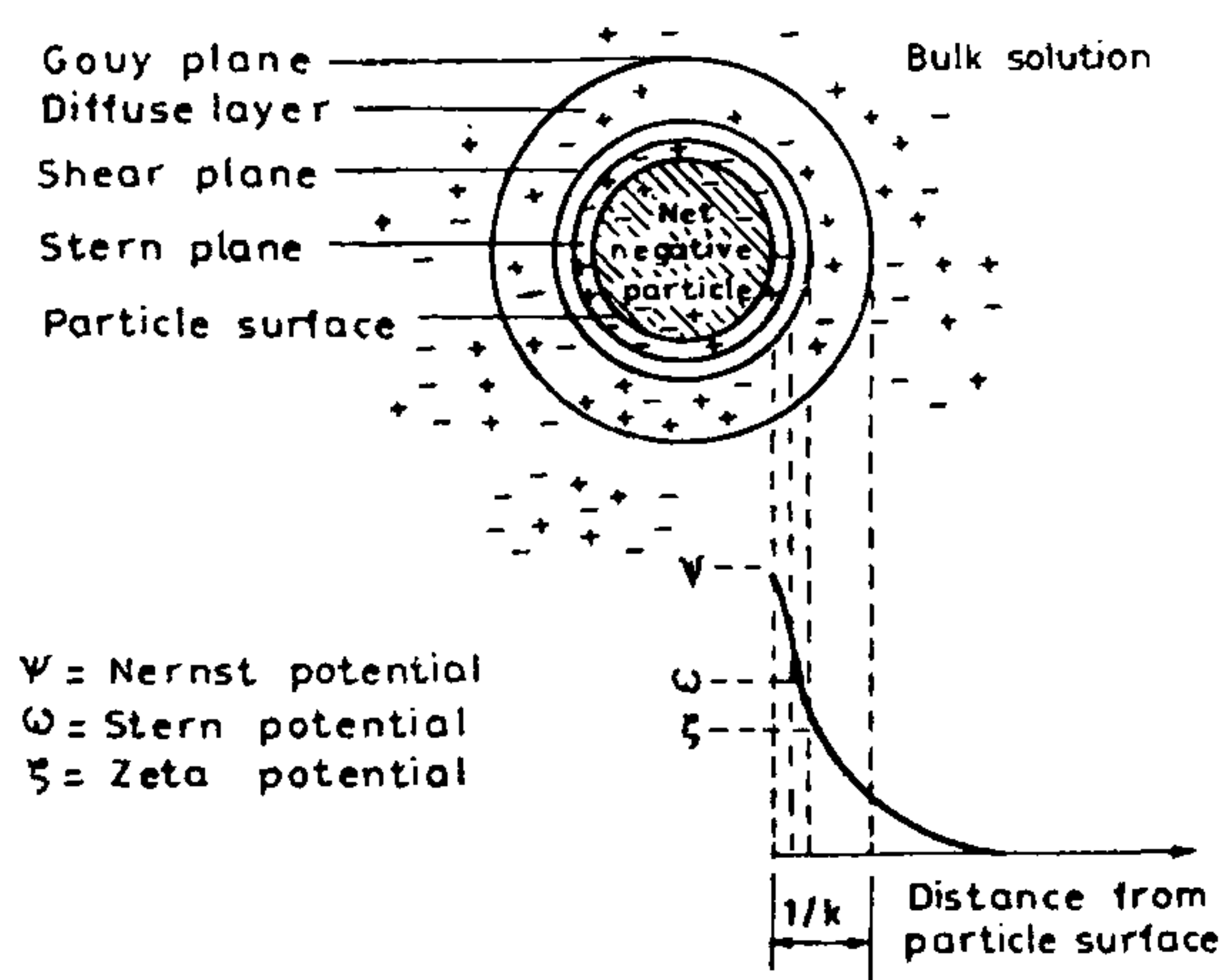


Figure 2. Electrical double layer (Priesing⁹).

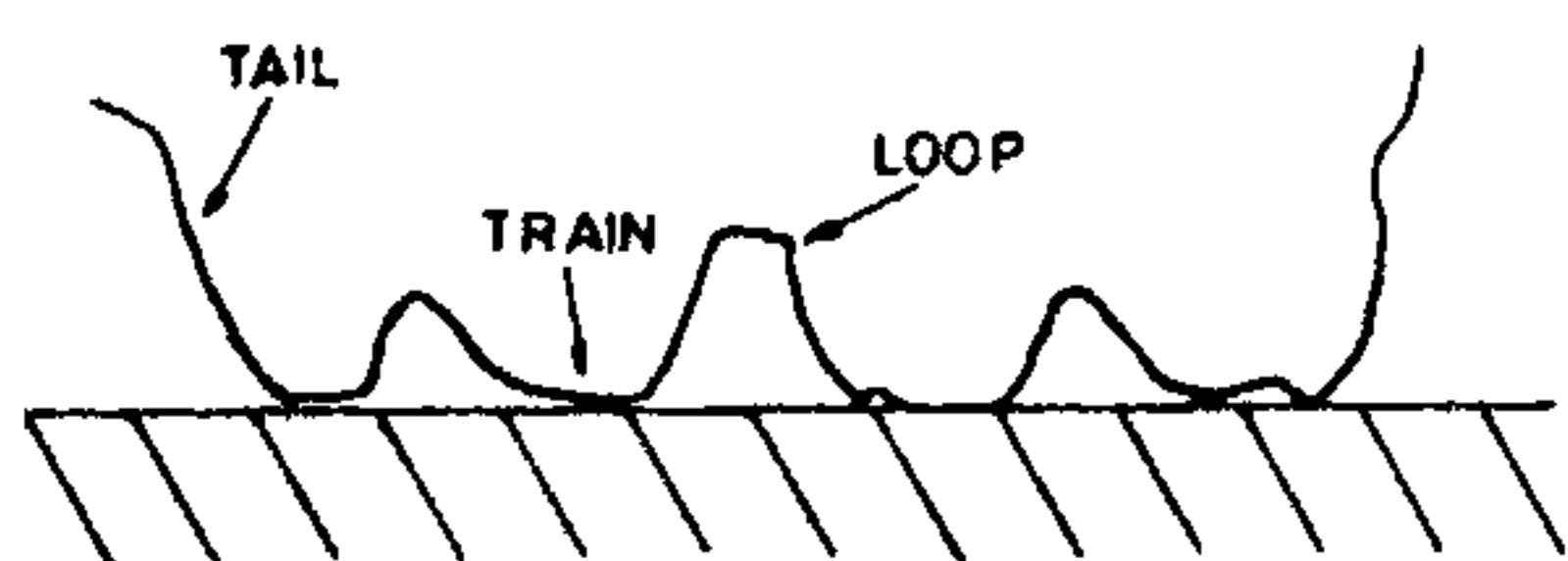


Figure 3. Configuration of an adsorbed polymer chain (G. J. Fleer *et al.* 1933).

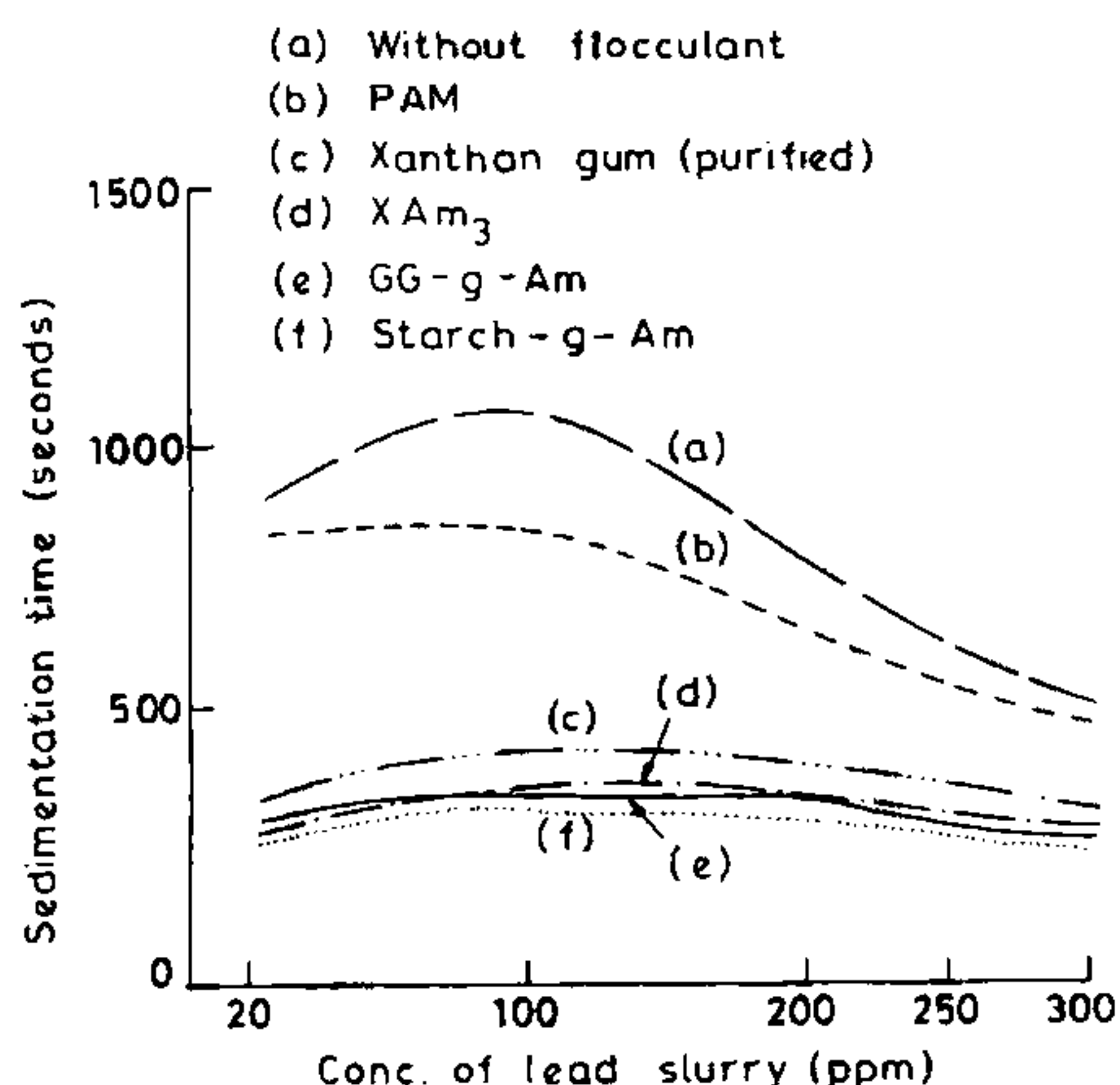


Figure 4. Variation of sedimentation time with concentration of lead slurry by addition of 2 ppm of various flocculants.

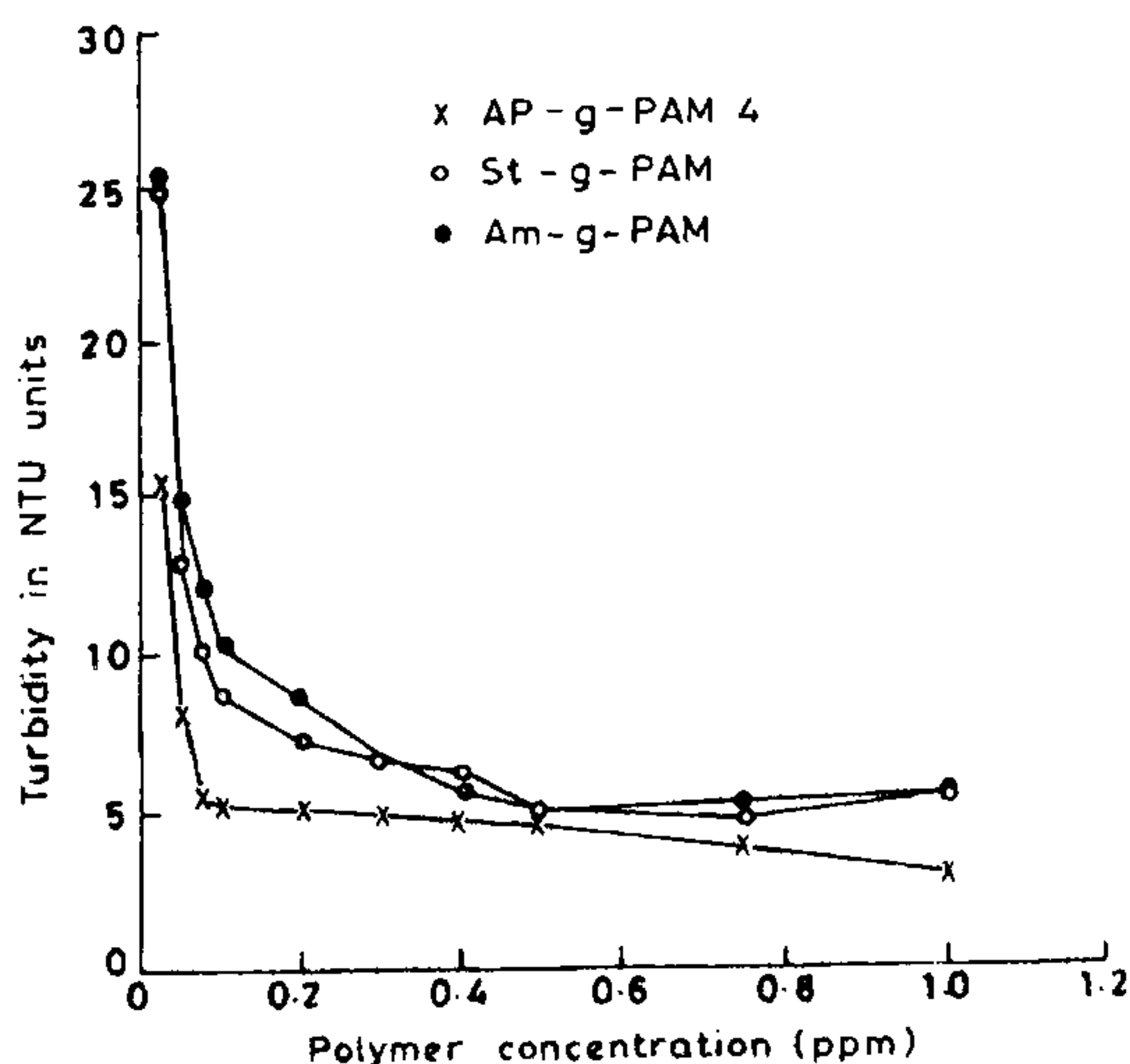


Figure 5. Variation of supernatant turbidity with flocculant dose in kaolin suspension (0.25%) in water: The comparison among Ap-g-PAM 4, St-g-PAM and Am-g-PAM. (Ref. 2 in *J. Appl. Polym. Sci.*, 1997, 66, 1721).

the Stern and diffusive layers is shown in Figure 2. Because of the repulsive forces between the particles, charged this way, the suspension can be stabilized⁹. Flocculation occurs due to this destabilization of the colloidal particles, by the addition of some water-soluble polymers.

Table 1. Flocculation characteristics of grafted polysaccharides in synthetic effluents

- The effect of molecular parameters of graft copolymers of guar gum and polyacrylamide (GM₁) was evaluated in the synthetic effluent of lead. The maximum efficiency was shown by GM₃, followed by GAM₁ and GAM₅^{29,30}. Among this series GM₃ has fewer but longer grafted chains of polyacrylamide. It appears that the presence of lead ions in the effluent, caused the straightening effect on the polymer chains. Due to this the polymer chain has not assumed globular form, thus making available all hydrogen bond-forming sites to participate in the flocculation by bridging mechanism. GAM₅ with more number of shorter grafts showed poor performance but still its flocculation efficiency was much higher than that of commercial polyacrylamide-based flocculant^{6,21,29,30}. The synthesis of GM₃ was scaled up and tested for various synthetic and industrial effluents^{29,30}. It was observed that GM₃ performs better than guar gum and commercial flocculant based on polyacrylamide (Figure 6).
- Among xanthan gum-g-acrylamides, (XM₃)^{16,17} is the most effective drag reducing having fewer but longer grafted polyacrylamide chains on xanthan gum backbone. Its synthesis was scaled up³¹. Its efficiency was tested in synthetic effluent containing lead and paper mill effluent. In lead effluent, its performance is better than commercial and purified xanthan gum and polyacrylamide. However the performance of GM₃ is better than XM₃ and reason for this observation has been discussed elsewhere^{6,17,21,31}. In paper mill effluent treatment, the polymer acts as flocculant and aids along with alum^{17,31}.
- Starch is used extensively for mineral treatment^{2,3,32-38}. Hence it was contemplated that grafted starch may have better performance as flocculant. As starch-g-acrylamide (SAM) has fewer and longer branches, it was chosen for scale up and testing for synthetic as well as industrial effluents. A comparative study⁶ was conducted for synthetic lead slurry. It has been found that this provides the best flocculating performance. At alkaline pH and higher shear rates, this flocculant performs better than the flocculants available commercially³⁸.
- Starch consists of a linear polymer amylose of low molecular weight (in range of 10,000–60,000) and branched amylopectin, which is major fraction of high molecular weight (in range of 50,000–10⁶). The performance of grafted amylose is inferior to grafted starch^{22,23,38}.
- A large number of graft copolymers of amylopectin and polyacrylamide were synthesized (Ap-g-PAM1, Ap-g-PAM8) and their flocculation efficiency has been evaluated in kaolin suspension, coal suspensions and paper mill effluent^{22,36,24}. It was found that Ap-g-PAM is the best flocculant (Figure 5) compared to St-g-PAM and Am-g-PAM. Enhanced efficiency of Ap-g-PAM is because of its greater degree of branching and higher molecular weight. Among the various graft copolymers, the one which has fewer but longer branch gives the best performance.
- A number of graft copolymers of sodium alginate and polyacrylamide (SAGI-SAGV) have been synthesized. Their performance is inferior to AP-g-PAM but their performance is better than many commercial flocculants. Similar is the performance of grafted CMC^{37,39}.
- When the grafted branches are partially hydrolysed in SAG-g-PAM, the performance increases to a certain level and then decreases. During hydrolysis, the grafted chains are straightened, due to electrostatic repulsion of negatively charged carboxylate anions. As a result, the approachability to the particles in a colloidal suspensions increases. There is an optimum degree of hydrolysis where grafted chains get straightened but have some degree of flexibility. Beyond the optimum level, the grafted chains lose their flexibility and behave like a rigid rod. As a result, flocculation performance decreases. Hence it is concluded that for efficient flocculation, the flexibility of grafted branches is necessary⁴⁰.

The major mechanisms of flocculation by polyelectrolytes are surface charge neutralization and bridging. Surface charge neutralization occurs if the charge of the flocculants is opposite in sign to that of the suspended particles. Addition of such a polymer to the suspension will result in aggregation caused by specific ion absorption. For neutral flocculants, the major mechanism of flocculation is the polymer bridging. The controversy concerning the bridging and charge neutralization mechanisms of aggregating aqueous suspensions by the adsorption of water soluble polymers is long standing. In their early experimental and theoretical investigations, Lamer and his school¹⁰ were prominent in advocating bridging. Hence there is no question that the bridging mechanism operates with uncharged polymers to the particles of the suspension. When very long polymer molecules are absorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may dangle. These loops and ends may come into contact with, and attach to, another particle forming a bridge between the two particles. This is the bridging mode of flocculation¹¹. Here charge of the particles/and or polymer do not play any important role.

The reason for better flocculating power of the graft copolymers over the linear polymers is as follows; essentially polymer bridging occurs because segments of a polymer chain absorb on different particles, thus linking the particles together. In order for effective bridging to

Table 2. Flocculation characteristics of grafted polysaccharides in industrial effluents

- For the industrial effluents containing nickel, copper and lead ions, the performance of grafted guar gum is better than that of guar gum and Tulespar (a commercial flocculant)^{29,30}.
- For industrial effluents from a copper industry (HCL, Ghatsila, India), the grafted starch (SAM-g-II) is better than Magnafloc-1011 at lower concentrations of the flocculant³⁸.
- In flocculation of hematite slimes, the grafted starch is found to be an efficient flocculant with small dose compared to Magnafloc-1011 in the normal and acidic pH range. At alkaline pH, grafted starch works even better than Magnafloc-101 (ref. 38).
- For flocculation of iron ore and Kiriburu slime pond overflows, greater settling rate of particles was observed using Magnafloc-1011 when flocculant dose was 30 ppm and pulp density 10% than that using Ap-g-PAM, SAM-II and SAG-II. However, at 10 ppm flocculant dose, the performance of Ap-g-PAM and SAM-II was better than other commercial effluents³⁵.
- Settling and filtration experiments were also performed with commercial and laboratory synthesized biodegradable flocculants on iron ore slimes. It is observed at flocculant dose of 10 ppm the settling performance of Ap-g-PAM and SAM-II was better than Magnafloc-1011 (Figure 7). In the filtration experiments, the performance of SAM-II is much better than SAG-II and Magnafloc-1011 at normal pH35 (Figure 8).
- The flocculation and settling characteristics of coking and non-coking coal suspensions were studied using biodegradable flocculants. The non-coking coals do not settle quickly and supernatant turbidity is quite high. Considering settling velocity and residual supernatant turbidity of the coal suspensions, the performance of Ap-g-PAM is better followed by St-g-PAM both for coking and non-coking coals³⁶ (Figure 9).

occur there must be sufficient chain lengths, which extend far enough from the particle surface to attach to other particles. In case of linear polymers, the polymer segments attached to the surface in trains, project into the solution as tails, or form part of loops, which links trains together¹². By this way they can form bridges between the colloidal particles to form flocs. This is shown in Figure 3. But for the graft copolymers, the dangling grafted chains can easily bind the colloidal particles through bridging to form flocs. This type of intense bridging is not possible in case of linear polymers.

Many graft copolymers have been synthesized by grafting polyacrylamide chains onto guar gum¹³⁻¹⁵, xanthan

gum^{16,17} carboxy methyl cellulose and starch¹⁸. Their shear stability and drag reduction efficiency have been extensively studied^{6,14}. It has been found that by varying the number and length of the grafted polyacrylamide chain onto the backbone, the graft copolymers having fewer and longer chains are more efficient as drag reducing agent¹³⁻¹⁹. Later on, the investigations on their flocculation ability yield the same pattern, i.e. the graft copolymers having fewer and longer grafted chains are found to be more effective flocculants⁶. Among the grafted guar gum, xanthan gum, carboxy methyl cellulose, sodium alginate and starch, it has been found that grafted starch is the most efficient flocculant^{6,20-25} (Figure 4). Starch

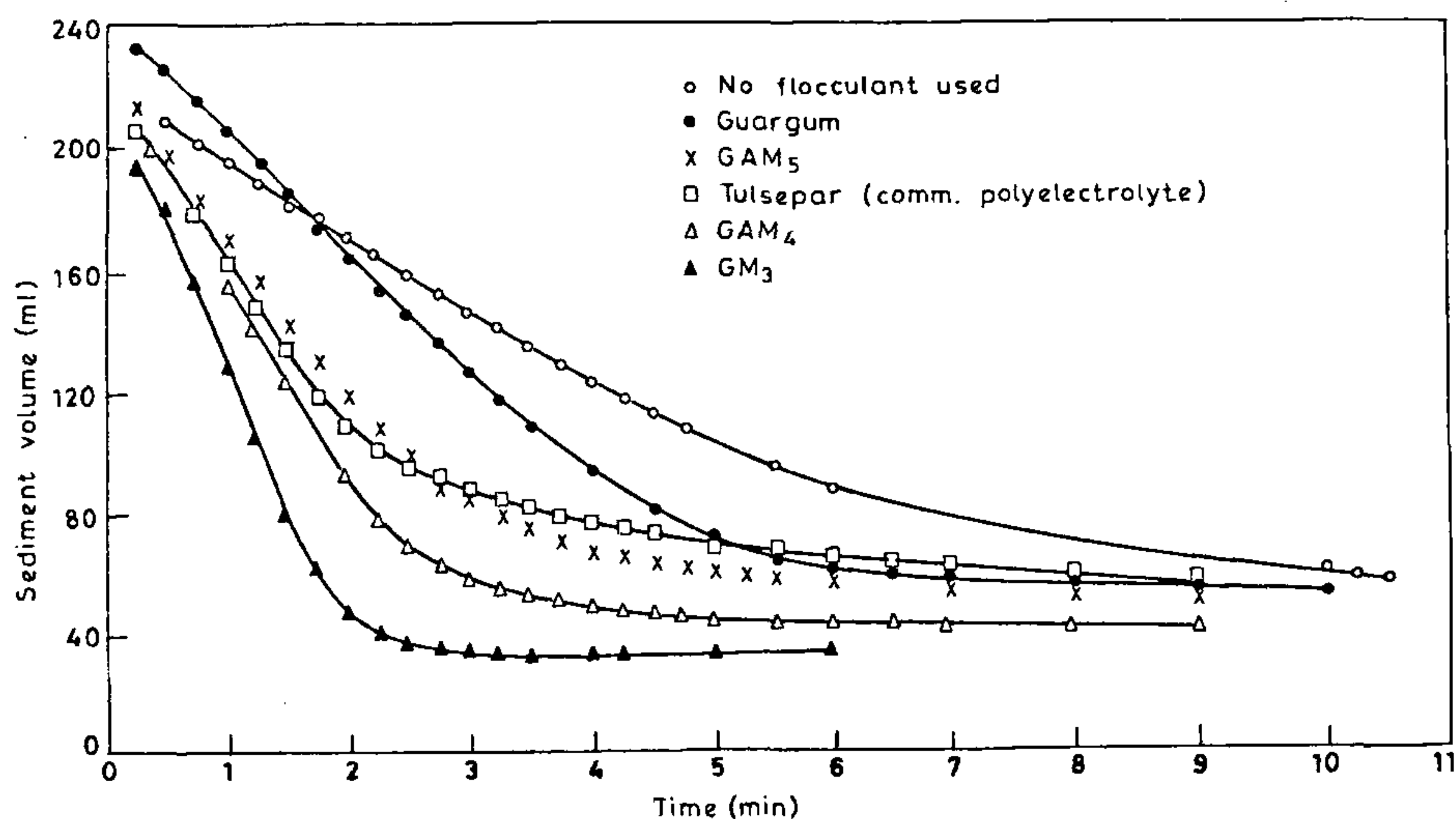


Figure 6. Effect of graft copolymers on flocculation of lead synthetic slurry.

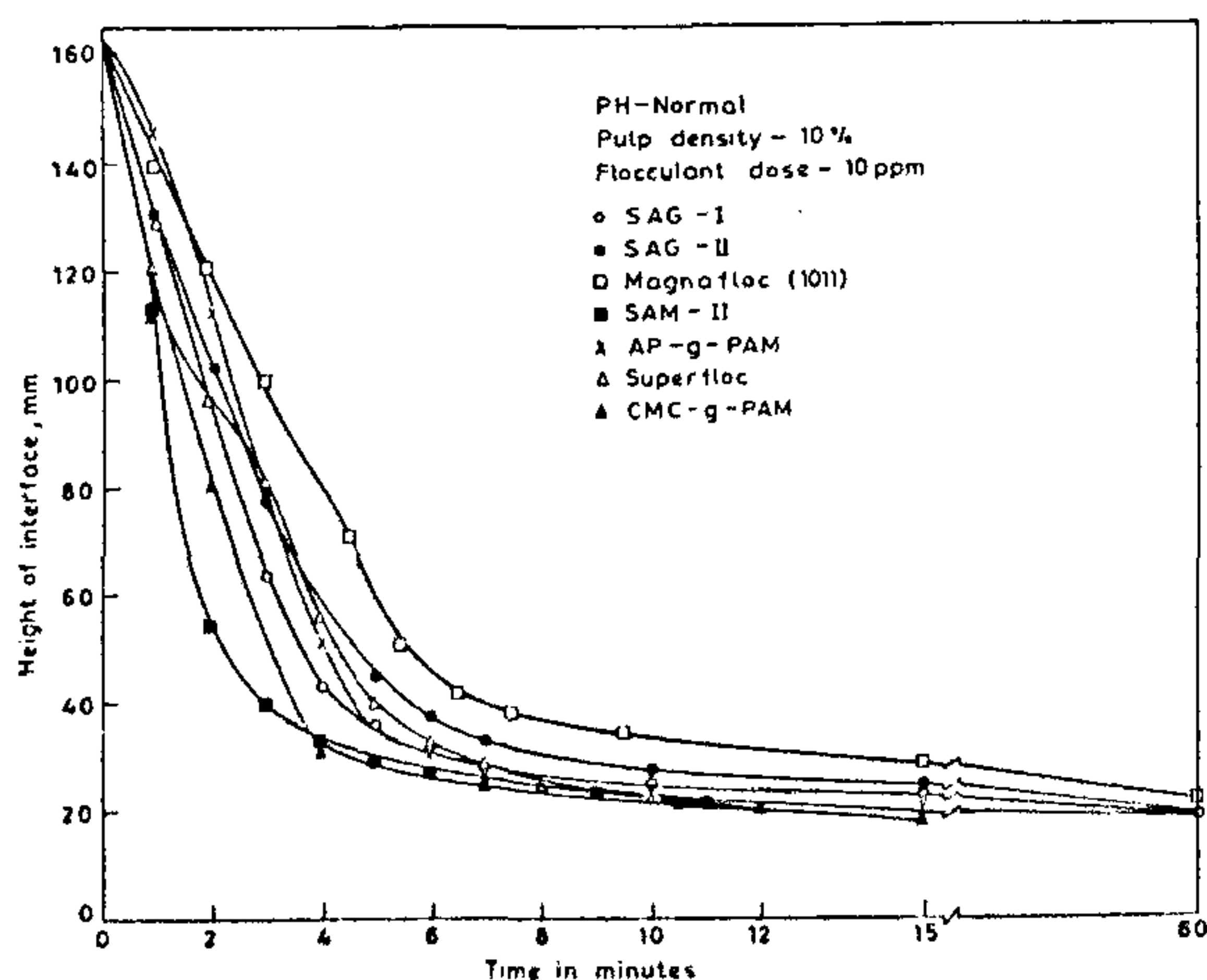


Figure 7. Variation of height of interface with time.

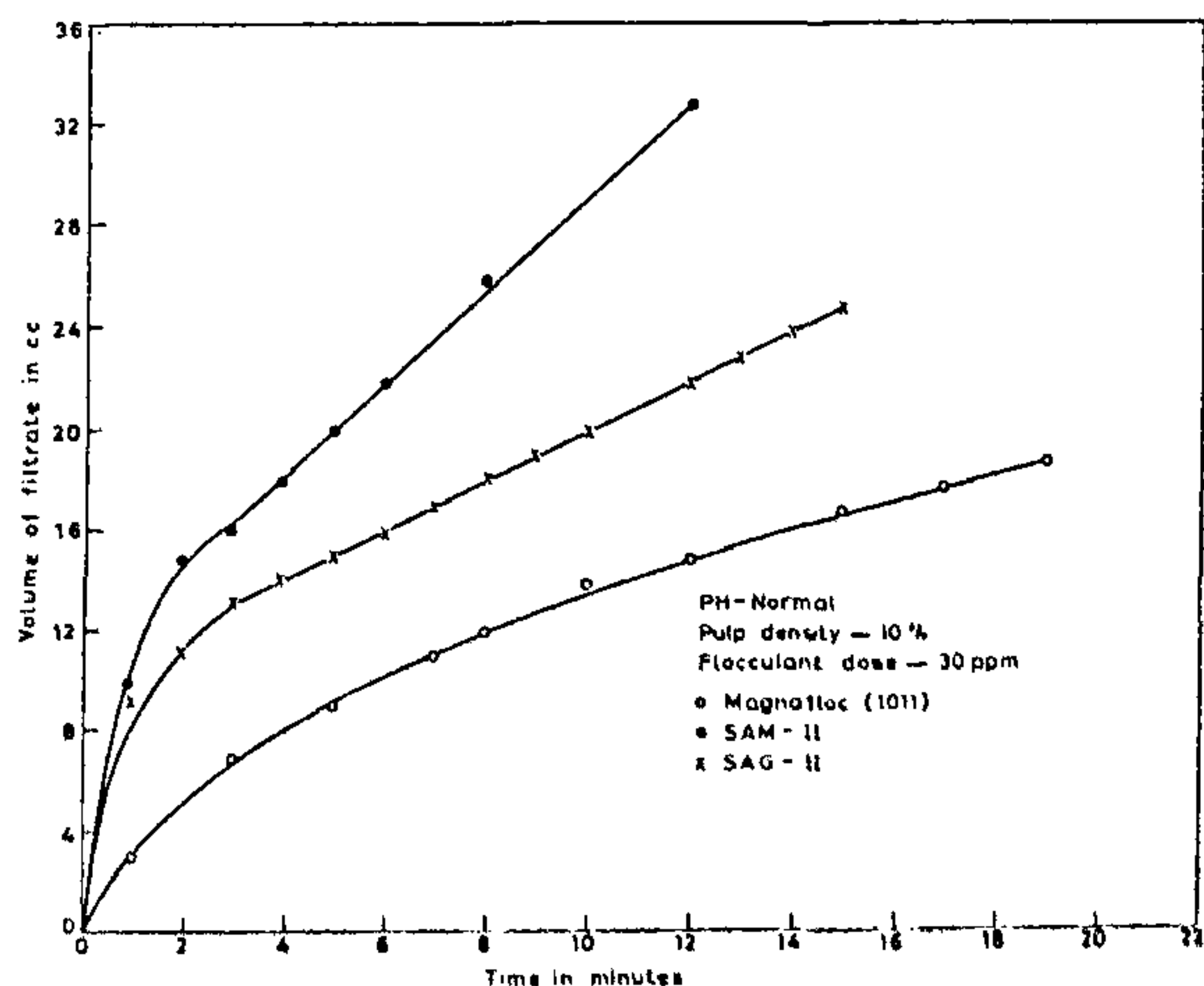


Figure 8. Variation of total volume of filtrate with time.

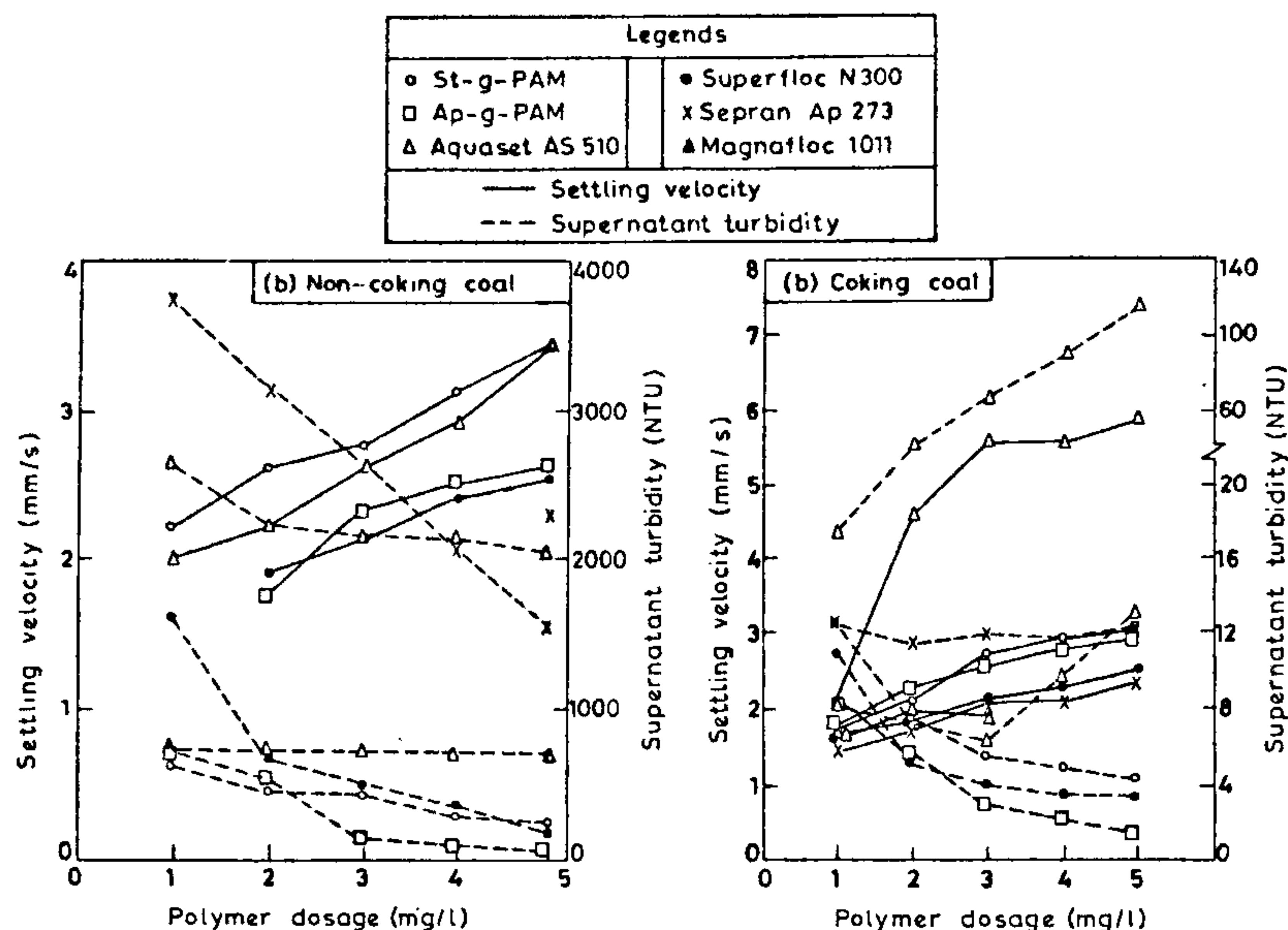


Figure 9. The settling velocity and turbidity versus polymer dosage.

consists of linear amylose (molecular weight 10,000–60,000) and branched amylopectin ($M_w = 50,000-10^6$). Hence amylose and amylopectin was grafted with polyacrylamide chains. Among all the polysaccharides, grafted amylopectin²²⁻²⁴ has been found to have best flocculation efficiency (Figure 5), giving credence to the proposed model⁶.

Most polysaccharides are purified before use⁷. The various graftcopolymers have been synthesized by ceric ion initiated solution polymerization technique¹³⁻²⁵. In this technique, the free radicals are formed exclusively on the polysaccharide molecules, thus minimizing the formation of homopolymers. Further, the acrylamide and ceric ammonium nitrate concentration was kept below 2.0 M within the limits of Owen and Shen²⁶ to ensure proper grafting. Graft copolymers are characterized²⁷ by viscometry, IR, NMR, thermal analysis, morphological study and XRD. Recently the proof of grafting has been given by enzyme hydrolysis²⁸.

Biodegradation can be followed by monitoring absolute viscosity at certain interval of times over entire period of the test at 30°C when bacterial activity is maximum. As mentioned earlier grafted polysaccharides are less prone to biological attack³⁰. The standard jar test and settling tests were followed for measurement of flocculation and settling characteristics²²⁻²⁴.

First the effectiveness as flocculant was measured in synthetic effluents of kaolin, $PbNO_3$ and coal. Later on industrial effluents from steel, copper, electroplating industries, iron ore mines and coal washeries were treated. In most cases, comparative studies were done with comm-

ercial effluents. The summary of above investigations is given in Tables 1 and 2.

On the basis of above discussion, it can be concluded that grafted polysaccharides are shear stable, efficient flocculating and settling aids for industrial effluent treatment and mineral processing. Of all the grafted polysaccharides, polyacrylamide grafted amylopectin having fewer but longer branches gives the best performance in a variety of synthetic and industrial effluents. As amylopectin itself is branched, its grafted chains will have more approachability to contaminants in the effluent⁶.

1. Bolto, B. A., *Progr. Polym. Sci.*, 1995, **20**, 987–1041.
2. Moody, G., *Mineral Engg.*, 1992, **5**, 479–492.
3. Bratby, J., *Coagulation and Flocculation*, Uplands Press Ltd, Cryodon, Cambridge, 1980, 1st edn.
4. Levine, S. and Friesen, W. I., in *Flocculation in Biotechnology and Separation Systems* (ed. Attia, Y. A.), Elsevier, Amsterdam, 1987, pp. 3–15.
5. Swanson, C. L., Shogren, R. L., Fanta G. F. and Imam, S. H., *J. Environ. Polym. Degradation*, 1993, **1**, 155–166.
6. Singh, R. P., *Advanced Turbulent Drag Reducing and Flocculating Materials Based on Polysaccharides in Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities* (eds Prasad, P. N., Mark, E. and Fai, T. J.), Plenum Press, New York, 1995, pp. 227–49.
7. Singh, R. P., Karmakar, G. P., Rath, S. K., Karmakar, N. C., Pandey, S. R., Tripathy, T., Kannan, K., Jain, S. K. and Lan, N. T., Based on Invited Talk, *Polymer Eng. Sci.*, 1999 (in press).
8. Stumm, W., Morgan, J. J., *JAWWA*, 1962, **54**, 971–991.
9. Priesing, C. P., *Indian Eng. Chem.*, 1962, **54**, 38–45.
10. Lamer, V. K. and Healy, T. W., *Rev. Pure. App. Chem.*, 1963, **13**, 112–133.
11. Ruehrwein, R. A. and Ward, A., *Soil Sci.*, 1952, **73**, 485.

12. Dickinson, E. and Eriksson, L., *Adv. Colloid Interface Sci.*, 1991, **34**, 1.
13. Deshmukh, S. R., Chaturvedi, P. N. and Singh, R. P., *J. Appl. Polym. Sci.*, 1985, **30**, 4013–4020.
14. Deshmukh, S. R. and Singh, R. P., *J. Appl. Polym. Sci.*, 1985, **30**, 4013–4020.
15. Deshmukh, S. R. and Singh, R. P., *J. Appl. Polym. Sci.*, 1987, **33**, 1963–1975.
16. Deshmukh, S. R. and Singh, R. P., *J. Appl. Polym. Sci.*, 1986, **32**, 6133–6177.
17. Ungeheur, S. R., Bewersdorff, H. W. and Singh, R. P., *J. Appl. Polym. Sci.*, 1989, **37**, 2933–2948.
18. Deshmukh, S. R., Sudhakar, K. and Singh, R. P., *J. Appl. Polym. Sci.*, 1991, **48**, 1091–1101.
19. Singh, R. P., in *Encyclopedia of Fluid Mechanics: Polymer Flow Engineering* (ed. Cheremisinoff, I. P.), Gulf Publishing, Houston, 1990, vol. 9, pp. 425–480.
20. Singh, R. P., *Popular Plastic Packaging*, 1994, **39**, 69.
21. Singh, R. P., Jain, S. K. and Lan, N., *Drag Reduction, Flocculation and Rheological Characteristics of Grafted Polysaccharides in Polymer Science Contemporary Themes* (ed. Sivaram, S.), Tata McGraw Hill, New Delhi, 1991, pp. 716–721.
22. Rath, S. K. and Singh, R. P., *J. Appl. Polym. Sci.*, 1997, **66**, 1721–1729.
23. Karmakar, G. P. and Singh, R. P., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1998, **113**, 119–124.
24. Rath, S. K. and Singh, R. P., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1998, **139**, 129–135.
25. Karmakar, N. C., Rath, S. K., Sastry, B. S. and Singh, R. P., *J. Appl. Polym. Sci.*, 1998, **70**, 2619–2625.
26. Owen, D. R. and Shen, T. C., in *Structure Solubility Relationship in Polymers* (eds Harris, F. W. and Seymour, R. P.), Academic Press, New York, 1977.
27. Rath, S. K. and Singh, R. P., *J. Appl. Polym. Sci.*, 1998, **70**, 1795–1810.
28. Rath, S. K. and Singh, R. P., *J. Appl. Polym. Sci.*, 1998, **70**, 2627–2633.
29. Kannan, K., M.Tech. thesis, IIT, Kharagpur, 1988.
30. Jain, S. K., M.Tech. thesis, IIT, Kharagpur, 1989.
31. Lan, N. T., M.Tech. thesis, IIT, Kharagpur, 1990.
32. Karmakar, G. P. and Singh, R. P., *Synthesis and Characterisation of Starch-g-Acrylamide Copolymers for Improved Oil Recovery*, SPE 37297, Houston, USA, 1996.
33. Karmakar, G. P. and Singh, R. P., *Synthesis and Application of Polymeric Flocculants for the Treatment of Paper Mill Effluents, Advances in Chemical Engineering*, Allied Publishers, New Delhi, 1996, p. 201.
34. Bhagat, R. P., Karmakar, G. P. and Singh, R. P., *Filtration of Iron Ore Slimes Using Synthesised Copolymer, Recent Advances in Metallurgical Processes*, New Age International, New Delhi, 1997, pp. 89–93.
35. Pandey, S. R., Tripathy, T., Bhagat, R. P. and Singh, R. P., *Behaviour of Iron Ore Slimes Using Various Polymeric Flocculants in Macromolecules, New Frontiers* (ed. Srinivasan, K. S. V.), Allied Publishers, New Delhi, 1998, pp. 1118–1121.
36. Karmakar, N. C., Sastry, B. S. and Singh, R. P., *Settling Characteristics of Coking and Non-Coking Coal Fines*, (ed. Srinivasan, K. S. V.), Allied Publishers, New Delhi, 1998, vol. 2, pp. 1114–1117.
37. Tripathy, T., Pandey, S. R., Bhagat, R. P. and Singh, R. P., (ed. Srinivasan, K. S. V.), Allied Publishers, New Delhi, 1998, vol. 2, 1084–1087.
38. Karmakar, G. P., Ph D thesis, IIT, Kharagpur, 1994.
39. Tripathy, T., Pandey, S. R., Karmakar, N. C., Bhagat, R. P. and Singh, R. P., *Eur. Polym. J.*, 1999, **35**, 2057–2072.
40. Tripathy Tridib and Singh R. P., *Eur. Polym. J.*, 2000 (in press).

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