

Settling Rates for Flocculation of Iron and Manganese Ore-Containing Suspensions by Cationic Glycogen

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Novel flocculants have been synthesized on the basis of glycogen. The efficiency of cationic glycogen can be explained in terms of Singh's qualitative easy approachability model (EAM). The jar test was used previously to evaluate flocculation efficacy, but we have recently shown that a plot of interface height vs. settling times provides a better measure. In accord with the EAM, a one-to-one correspondence between settling velocity and radius of gyration of flocculants in various solutions has been demonstrated, providing quantitative proof of the EAM. Now the flocculation efficacy of cationic glycogen is evaluated by determination of settling times in both iron and manganese ore suspensions and compared with the performance of other polymer flocculants. Its superior flocculation efficacy over commercial flocculants and other flocculants synthesized by us is demonstrated. POLYM. ENG. SCI., 48:1892-1896, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

There is a difficulty in the basic process of getting solid constituents out of a liquid solution or suspension. Fine particles with diameters on the order of 10 μm will not settle out of suspension by gravity alone in an economically reasonable amount of time. Addition of flocculants to liquid suspensions causes aggregation of particles in so-called flocs, thereby increasing the ease of their removal.

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Since fresh water is a scarce commodity in many societies—and a valuable one in all nations—reusage of industrial water and municipal sludges can have a powerful impact on the economy and environment. While water used for direct human consumption and for agriculture cannot be recycled, water used for industrial processes can be reused successfully if purified; and purification is dependent on getting the solid constituents out of suspension without imposing excessive cost. Around the world the application of synthetic flocculants is accepted for solid–liquid separation in the recycling of domestic wastewater and of industrial and mineral processing effluents [1–3].

Flocculation, contrasted with coagulation, does not rely solely on manipulation of electric charges. Polymers are effective and convenient flocculants: they can be used in small quantities (1–5 ppm) and form flocs that are larger, stronger, and better settling than simple coagulation electrolytes. Based on the easy approachability model (EAM), the most effective flocculants are those that allow suspended particles to easily approach the polymer flocculant [4–6].

Synthetic polyacrylamides are effective flocculants and easily tailored by controlling the molecular weight and weight distribution, the chemical structure of the polymers, and the nature and ratio of functional groups on the polymeric backbone. However, the synthetic polymer flocculants are not shear resistant or biodegradable [1]. By contrast, naturally occurring polysaccharides are shear stable, biodegradable, cheap, and easily available from reproducible farm and forest resources [7, 8]; yet they are less efficient flocculants and have a shorter shelf-life due to biodegradability [1].

We have shown that grafting synthetic polymers onto a polysaccharide backbone can result in an improved flocculant [9] as well as a better drag reducing agent [10]. Polyacrylamide-grafted polysaccharides are nonionic and

TABLE 1. Details of synthesis of cationic polysaccharides.

Polymer	Amount of AGU ^a (mol)	Amount of CHPTAC (mol)	Volume of NaOH (mol)	Temp. (°C)	Time (h)	Intrinsic viscosity (dL g) ⁻¹
Cat AP3	0.0123	0.0119	0.015	40–50	18	8.0
Cat AM	0.0185	0.0106	0.015	40–50	18	9.3
Cat Gly4	0.0092	0.0066	0.015	40–50	18	7.4
Cat GG4	0.0061	0.0066	0.015	40–50	18	15.6
Cat St3	0.0092	0.0066	0.015	40–50	18	8.7

^a 1 mol Anhydroglucose Unit (AGU) = 162 g.

therefore perform best in industrial effluents containing contaminant particles of relatively low negativity. Where colloidal particles are highly negatively charged, cationic polymers are more efficient [11].

Highly charged cationic polymers such as polyimines and polyamines are expensive. Such cationic polymers are being used in waste water carrying high negative charges and are widely used as wet-end additives in paper industry [12–14]. One of us previously demonstrated that cationized polysaccharides exhibit higher flocculation than the corresponding unmodified polysaccharides [1, 15]. Among various water-soluble polysaccharides, glycogen is most highly branched and has high molecular weight [16, 17]. In view of the authors' earlier findings, five polysaccharides were chosen as base polymers for creating reactive cationic moieties via a quaternary ammonium compound.

Previously, we evaluated flocculation efficacy of our modified polysaccharides by the jar test. In the so-called jar test, the turbidity of suspensions is measured as a function of polymer concentration. Experimental accuracy is not high; the often concave resultant curves sometimes exhibit minima and/or maxima [18].

A better measure of flocculation is based on interface height plotted as a function of settling times. Introduction of a flocculant into a container of suspension medium causes an interface to form: above it is the supernatant liquid and below is the suspension containing contaminants. As flocculation occurs via the flocculating agent, the interface descends until solids are settled at the bottom. Curves are linear except for a final short region that is concave [3]. The linear part gives us the settling velocities y .

A cationized glycogen was previously synthesized and analyzed by the jar test in iron ore suspensions. Here we analyze by measurements of settling velocities the performance of cationic glycogen as a flocculant in suspensions of Fe and Mn ores. The flocculation efficacy is compared to that of other cationic polysaccharides and to several commercially available flocculants.

MATERIALS

Flocculants

Amylopectin (AP), amylose (AM), and glycogen (Gly) were purchased from Sigma Chemicals, USA. Starch (St)

was supplied by E. Merck (India) Limited, Bombay. Guar gum (GG) was a gift from Hindustan Gum & Chemicals, India. All of these polysaccharides have been cationized (Cat) by a reaction with *N*-(3-chloro-2-hydroxypropyl)trimethyl ammonium chloride (CHPTAC) (Lancaster Synthesis Company, England). The synthesis is described in [1] and [15] while a very detailed description is provided in a thesis by one of us [18]. Varying amounts of CHPTAC were used to give different degrees of cationization of the starting polymers. Those with the best flocculation efficacy—and thus studied further—are described by the following notation: Cat AP3, Cat AM, Cat Gly4, Cat GG4, and Cat St3 [1, 15, 18]. Relevant parameters of the synthesis are given in Table 1. Viscosity measurements of dilute aqueous solutions of the polymers were conducted at 25°C using an Ubbelohde viscometer.

Five commercial flocculants were tested. Magnafloc 351 (Mag 351), Magnafloc LT 22 (Mag LT22), and Magnafloc 156 (Mag 156) were from Ciba Specialty Chemicals, UK. Rishfloc 440 HV (Rish 440 HV) and Rishfloc 226 LV (Rish 226 LV) were from Rishabh Metals and Chemicals, Bombay.

Suspensions

Two types of suspensions were used: iron and manganese ores (gifts from Joda Mines, Jharkand, India). Details of the compositions are provided in Table 2. Density was determined using a specific gravity bottle by the standard method. Particle size was determined with a Malvern 3601 Particle Size Analyzer (manufactured in England). Zeta potential was measured by Particle Micro Electrophoresis (Apparatus Mark II, manufactured in England) at pH = 7.0.

EXPERIMENTAL PROCEDURES

Flocculation efficacy was determined by a comparison of settling velocities. The settling test was conducted in a 100-mL stoppered graduated cylinder, and settling times were recorded with a stopwatch. First the cylinder was filled with the suspension sample and then the polymer flocculant was added to it. Polymer concentration was 6 ppm for Fe ore suspensions and 9 ppm for Mn ore suspensions. The cylinder was inverted 10 times for thorough

TABLE 2. Composition and properties of ore suspensions.

Suspension	Composition						Particle size (nm)	Sp. Gravity (g cc) ⁻¹	Zeta potential (mV)
	% Mn	% Fe	% Al ₂ O ₃	% SiO ₂	% P	% Moisture			
Fe ore	—	56.37	7.01	7.48	0.2	9.5	105.7	3.45	-32.45
Mn ore	45	16	8	6	0.12	8	86.9	2.5	-32

mixing. Afterward the cylinder was set upright and the height of interface between water and the settling solid bed was measured over time. As described already in the Introduction, interface height of the flocculant-containing suspension (of Fe or Mn ores) was measured as a function of time and plotted. The slopes of the linear portion give the settling velocities in cm s⁻¹.

Results for Fe Ore Suspensions

The flocculation efficacy for five different cationic polysaccharides in iron ore suspension is demonstrated in Fig. 1. The plot of interface height as a function of settling time indicates that settling velocity is highest for the Cat Gly4 flocculant and lowest for Cat AM (Table 3). Figure 2 shows a similar plot comparing our cationized glycogen to several commercial flocculants.

Results for Mn Ore Suspensions

For the same flocculants in a Mn ore suspension, results are shown in Figs. 3 and 4. Cat Gly4 has the highest settling velocity among the various cationized polysaccharides. It performs well also compared to commercial flocculants; one of these (Mag 351) has a higher settling velocity.

Numerical values for the settling velocities, molecular weight, and radius of gyration (in aqueous suspension) for the various flocculants are reported in Table 3. The weight average molecular weights M_w and also radii of gyration R_G were determined by static light scattering analysis using a DLS-7000 Super Dynamic Light Scattering Spectrometer (Otsuka Electronics, Hirakata-City, Osaka, Japan). R_G values were obtained using the procedure developed originally by Bruno Zimm and described by Gedde [19].

DISCUSSION

Flocculants in Figs. 1–4 have been evaluated previously by the jar test in iron ore suspension [1] and manganese ore suspension [18]. In a comparison among our modified polysaccharides and among commercial flocculants, Cat Gly4 exhibited the highest flocculation efficacy, demonstrated by the resultant low turbidity of the suspension. In Figs. 1 and 2, we demonstrate that we have achieved the same results by the method of recording settling times for the flocculants in Fe ore suspensions.

Similarly, Cat Gly4 has the best flocculation efficacy among the cationic polysaccharides when tested in a Mn ore suspension (see Fig. 3). Compared to commercial flocculants, only Mag 351 has a higher settling velocity in the Mn ore suspension. How do we explain this behavior?

From the negative values of zeta potential (Table 2), it is clear that both ore suspensions carry a substantial negative charge. Thus, cationic flocculants are most effective. Additionally we know that a flocculating agent is expected to be also a drag reduction (DR) agent. A model of DR developed earlier assumes that each polymer chain pervades a volume in the liquid medium exceeding the dimensions of that chain [20, 10]. This explains DR efficacy at low concentrations such as 10 ppm. Flocculating agents are effective also at such low concentrations. A commonly available measure of pervaded volume is the radius of gyration R_G . We have established a relationship between the settling velocity y and R_G [3]. Namely, there is a one-to-one correspondence in the form of a power law relationship:

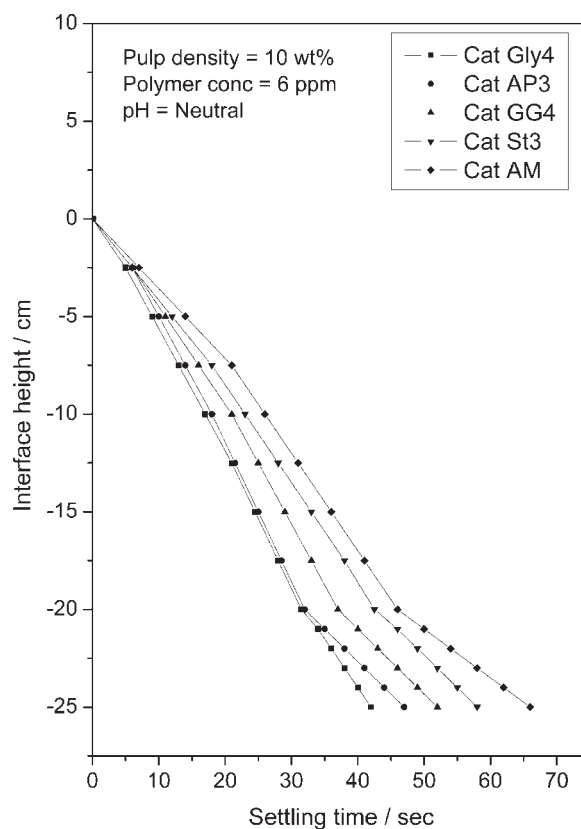


FIG. 1. Settling times of cationic polysaccharides in Fe ore suspension.

TABLE 3. Properties of flocculants in Fe and Mn ore suspensions.

Polymer	M_w (weight average) $(g\ mol)^{-1}$	R_G (nm)	Settling velocity in Fe ore suspension $(cm\ s)^{-1}$	Settling velocity in Mn ore suspension $(cm\ s)^{-1}$
Cat AP3	2.64E + 06	81.9	0.62	1.08
Cat AM	6.90E + 04	9.2	0.43	0.61
Cat Gly4	6.81E + 06	108.0	0.64	1.25
Cat GG4	6.60E + 05	44.0	0.54	0.90
Cat St3	4.33E + 05	21.5	0.47	0.76
Mag 351	1.44E + 07	128.2	0.60	1.37
Mag LT 22	4.76E + 06	97.5	0.52	0.83
Mag 156	6.56E + 05	91.9	0.51	0.60
Rish 226 LV	3.27E + 05	95.6	0.44	0.51
Rish 440 HV	1.16E + 05	11.6	0.48	0.58

$$y = aR_G^b \quad (1)$$

where R_G is the root-mean-square distance of the collection of atoms from their common center of gravity (see for instance Gedde [19] or Lucas and her colleagues [21]):

$$R_G^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i} \quad (2)$$

Here m_i is the mass of the i -th atom while r_i is the vector from the center of gravity to that atom; the summations cover all atoms. Values for a and b for Fe ore

and Mn ore suspensions determined previously [3] are $a = 0.632$ and $b = 0.174$ in Fe ore and $a = 1.181$ and $b = 0.291$ in Mn ore (where values for y were in $nm \times 10^{-2}$). We need to keep in mind also that R_G is proportional to the square root of the degree of polymerization (i.e. molecular weight). Molecular weights and R_G values for our cationic polysaccharides and for the commercial flocculants are listed in Table 3.

In light of Eq. 1 and Singh's EAM, we have an explanation for the high flocculation efficacy of Cat Gly4. Cationic glycogen has the highest molecular weight among the various polysaccharides (Table 3). Its highly branched structure along with its comparatively high radius of gyration would predict, based on Eq. 1 and the EAM, easier approachability of particles and a higher settling velocity. This is the behavior observed for Cat Gly4 compared to

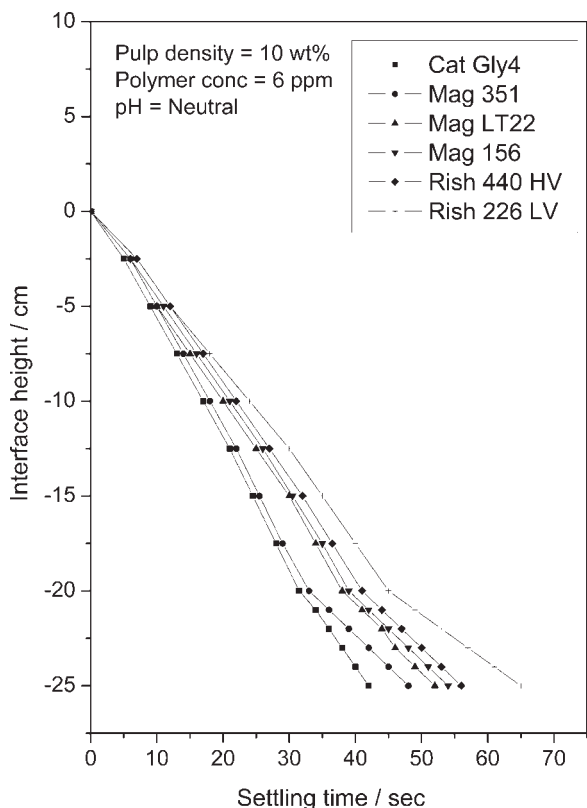


FIG. 2. Settling time of cationic glycogen compared to that of commercial flocculants in Fe ore suspension.

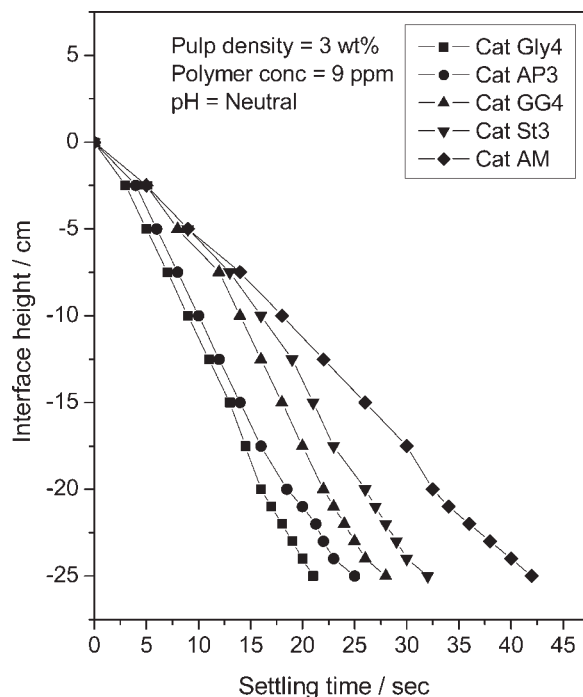


FIG. 3. Settling times of cationic polysaccharides in Mn ore suspension.

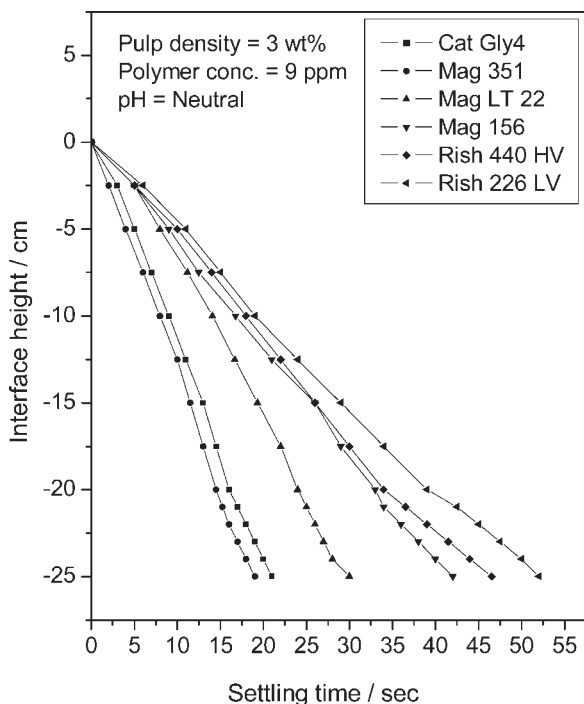


FIG. 4. Settling time of cationic glycogen compared to that of commercial flocculants in Mn ore suspension.

other cationic polysaccharides in iron ore suspension (see Fig. 1) and also in manganese ore suspension (see Fig. 3).

Compared to commercially available flocculants, Cat Gly4 has the highest settling velocity in iron ore suspension. However, in the Mn ore suspension, the cationic flocculant Mag 351 has a slightly higher settling velocity (Fig. 4 and Table 3). Here the y versus R_g curves defined in [3] and based on Eq. 1 are instructive. First, we note that the R_G of Mag 351 (128.2 nm) is higher than that for Cat Gly4 (108.0 nm). Next, based on values of a and b for Eq. 1, it is clear that the shape of the curves is different for flocculants in Mn ore versus Fe ore suspension. Indeed, the y versus R_g curve for Fe ore is nearly flat above $R_G = 80$ nm, hence the close values of settling velocity for Cat Gly 4 ($y = 0.64$ cm s⁻¹) and Mag 351 ($y = 0.60$ cm s⁻¹). By contrast, the same curve for Mn ore is still increasing according to Eq. 1 at R_G values above 80 nm. Thus the settling velocity for Mag 351 is slightly higher ($y = 1.37$ cm s⁻¹) than that for Cat Gly4 ($y = 1.25$ cm s⁻¹).

SUMMARY

We have confirmed the predictability of settling velocity of flocculants by their radii of gyration. Further, we have shown that a modified polysaccharide (cationic glycogen) synthesized by us performs almost as well as or better than commercial flocculants in suspensions containing a large degree of negatively charged particles. Finally, for reasons mentioned in the Introduction, our modified polysaccharide also has economic advantages over synthetic commercial flocculants.

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REFERENCES

1. R.P. Singh, G.P. Karmakar, S.K. Rath, N.C. Karmakar, S.R. Pandey, T. Tripathy, J. Panda, K. Kannan, S.K. Jain, and N.T. Lan, *Polym. Eng. Sci.*, **40**, 46 (2000).
2. B.A. Bolto, *Prog. Polym. Sci.*, **20**, 987 (1995).
3. F.A. Rey and R.C. Varsanik, "Application and Function of Synthetic Polymeric Flocculants in Wastewater Treatment," in *Water Soluble Polymers Beauty with Performance*, J.E. Glass, Ed., American Chemical Society, Washington, DC (1986).
4. S. Pal, D. Mal, and R.P. Singh, *Colloid Surf. Physicochem. Eng. Aspect.*, **289**, 193 (2006).
5. R.P. Singh, "Flocculation," in *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities*, P.N. Prasad, J.E. Mark, and T.J. Fai, Eds., Plannum Publishing Corporation, New York, 227 (1995).
6. W. Brostow, S. Pal, and R.P. Singh, *Mat. Lett.*, **61**, 4381 (2007).
7. H. Barkert and J. Hartmann, "Flocculants," in *Encyclopedia of Industrial Chemistry*, 5th ed., VCH, Weinheim, **11A**, 251, (1988).
8. R.P. Singh, T. Tripathy, G.P. Karmakar, S.K. Rath, N.C. Karmakar, S.R. Pandey, K. Kannan, S.K. Jain, and N.T. Lan, *Curr. Sci.*, **78**, 798 (2000).
9. R.P. Singh, B.R. Nayak, D.R. Biswal, T. Tripathy, and K. Banik, *Mater. Res. Innovat.*, **7**, 331 (2003).
10. W. Brostow, H.E.H. Lobland, T. Reddy, R.P. Singh, and L. White, *J. Mater. Res.*, **22**(1), 56 (2007).
11. H.A. Ellis, S.I. Utah, A. Ogunrinde, and M.O. Ogedengbe, *Water Res.*, **16**, 1433 (1982).
12. W. Nachtergaele, *Starch/Stärke*, **41**, 27 (1989).
13. H. Grano, J.Y. Kauhaluoma, T. Suortti, J. Kaki, and K. Nurmi, *Carbohydr. Polym.*, **41**, 277 (2000).
14. A. Larsson and M. Rasmusson, *Carbohydr. Res.*, **304**, 315 (1997).
15. S. Pal, D. Mal, and R.P. Singh, *Carbohydr. Polym.*, **59**, 417 (2005).
16. M. Matsui, M. Kakut, and A. Misaki, *Carbohydr. Polym.*, **31**, 227 (1996).
17. D.J. Manners, *Carbohydr. Polym.*, **16**, 37 (1991).
18. S. Pal, Synthesis, Characterization, Flocculation and Rheological Characteristics of Cationic Polysaccharides, PhD Thesis, Indian Institute of Technology Kharagpur (2005).
19. U.W. Gedde, *Polymer Physics*, Springer, Berlin, New York (2002).
20. W. Brostow, *Polymer*, **24**, 631 (1983).
21. E.F. Lucas, B.G. Soares, and E. Monteiro, *Caracterização de Polimeros*, e-papers, Rio de Janeiro (2001).