International Journal of Biological Macromolecules 72 (2015) 356–363

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Modified amylopectin based flocculant for the treatment of synthetic effluent and industrial wastewaters

Amit Kumar Sarkar [a], Soumitra Ghorai [a], Abhay Shankar Patra [a,b], Brijesh K. Mishra [c], N.R. Mandre [d], Sagar Pal [a,*]

[a] Polymer Chemistry Laboratory, Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India
[b] Tata Steel R&D, Jamshedpur, India
[c] Department of Environmental Science & Engineering, Indian School of Mines, Dhanbad 826004, India
[d] Department of Fuel & Mineral Engineering, Indian School of Mines, Dhanbad 826004, India

ARTICLE INFO

Article history:
Received 20 June 2014
Received in revised form 4 August 2014
Accepted 7 August 2014
Available online 23 August 2014

Keywords:
Amylopectin
Flocculation
Industrial wastewater

ABSTRACT

Herein, we report the application of an efficient polymeric flocculant based on amylopectin grafted with poly (acrylic acid) (g-AP) for the treatment of synthetic effluent as well as various industrial wastewaters. The flocculation characteristics of g-AP have been explored in different pH conditions using silica suspension by measurement of residual turbidity as well as floc size. Results suggest that in acidic pH, patching mechanism is predominating while at neutral and alkaline pH, bridging is the main mechanism. In addition, aggregation of particles and particle collision models confirm that bridging mechanism is the key mechanism at alkaline condition. Further, g-AP demonstrates excellent potential as flocculant for the treatment of paper effluent, textile wastewater and shows better flocculation performance than that of commercially available flocculant. Besides, the pilot scale study of mine processwater suggests excellent efficacy of g-AP as flocculant.

1. Introduction

Recycling of industrial wastewaters as well as mineral processing effluents is very crucial, in particular to meet the requirement of potable, industrial as well as agricultural water [1]. Various efforts have been made in past by different research groups to reuse the industrial wastewaters after proper treatment [1–3]. The primary treatment of wastewater mainly requires the removal of discarded contaminants, toxic heavy metals, aromatic compounds and so on [4,5]. Flocculation is a process which involves the formation of aggregates and settles down the colloidal particles. It is consider as the most efficient technique for the primary treatment of wastewater [1].

In recent years, more attention has been focused towards modified natural polymers, in particular by grafting suitable synthetic polymer chains on natural polysaccharide backbone, mainly because of its better approachability towards the contaminant particles as explained by Singh & his coworkers [1,6–10]. Moreover, based on the substituent groups present in the copolymer structure, patching, charge neutralization or bridging are the main mechanisms in flocculation process [5,11–13]. For example, flocculants which carry carboxylate or quaternary ammonium groups, charge neutralization mechanism is predominating [5]. In contrast, flocculants having high molecular weight mainly follow bridging mechanism. In patch flocculation, local charge reversal was occurred on the patches during electrostatic attraction between the oppositely charged particles [11]. Since wastewaters eluted from various industries have different pH, so it is essential to investigate the flocculation characteristics in various pH conditions.

Recently, in our laboratory, a series of high performance biodegradable graft copolymers have been developed based on amylopectin and poly (acrylic acid) (g-AP) by varying the reaction parameters [14]. This article reports the detailed application of g-AP as an efficient flocculant for the treatment of various industrial effluents along with pilot scale study for the treatment of mine processwater. Besides, textile wastewater may contain cationic as well as anionic dyes and thus we have also investigated the flocculation characteristics of g-AP using methylene blue (MB) as cationic dye and reactive blue (RB) as anionic dye in different pH conditions. The flocculation characteristics were also performed in silica suspension, in particular by varying the pH of the media to explain the flocculation mechanism.

* Corresponding author. Tel.: +91 326 2235769; fax: +91 326 2296615.
E-mail addresses: pal.s.ac@ismdhanbad.ac.in, sagarpal1@hotmail.com (S. Pal).

http://dx.doi.org/10.1016/j.ijbiomac.2014.08.019
0141-8130/

2. Materials and methods

2.1. Materials

Poly (acrylic acid) grafted amylopectin (g-AP) as synthesized earlier [14] was used for flocculation study. Hydrochloric acid (E. Mark, Mumbai, India), sodium hydroxide (E. Mark, Mumbai, India), MB (Loba Chemie Pvt. Ltd., Mumbai, India), RB (received as gift sample from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana) were of analytical grade and used as received. Silica was used as synthetic effluent.

The commercial flocculant (namely FL-910 SNF, anionic in nature, $M_w = 4.35 \times 10^6$ g mol^{-1}) was collected as gift sample from Tata Steel (R&D), Jamshedpur, India. Paper effluent was collected from a paper industry near to Triveni, Hooghly, India. Textile wastewater was acquired from a textile industry near to Ranchi, India. The lab scale as well as pilot scale study of mine processwater was carried out at Tata Steel R&D, Jamshedpur.

2.2. Preparation of g-AP

g-AP was synthesized using free radical polymerization technique in inert atmosphere of nitrogen, where potassium persulphate (KPS) was used as initiator [14]. The required amount of amylopectin was dissolved in 85 mL water. The AP solution was poured in a three necked flask, which was already fitted with a nitrogen source. After addition of initiator and monomer solutions, the grafting reaction was continued for 1 h at a temperature of 65 ± 1 °C in inert atmosphere. Finally the polymerization reaction was terminated using hydroquinone solution [14]. By varying the reaction parameters, various g-APs were prepared. The optimized one (g-AP 5) was selected through its higher % GE and intrinsic viscosity [14].

2.3. Gel characteristics of g-AP

The gel properties of AP and g-AP were investigated by determining the storage modulus (G') and loss modulus (G''). 1 wt% solutions of AP and g-AP were prepared at *pH* 7.4 buffer media. The rheological measurements were carried out using Bohlin Gemini-2 rheometer (Malvern, UK) with varying shear stress (σ) at 37 ± 1 °C with a constant frequency of 0.5 Hz. Also, frequency sweep measurements were executed in the frequency range from 0.01 to 10 Hz at a constant stress of 0.001 Pa.

2.4. Investigation of flocculation characteristics by silica suspension

2.4.1. Flocculation characteristics using silica suspension

The standard jar test procedure was used to flocculate the silica particles in various pH conditions using a flocculator (Make: Gon Engineering Works, Dhanbad, India) and a turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). The silica suspension was prepared by mixing 1 g silica in 400 mL distilled water. Then the suspensions were taken in a 1-L beaker. After the addition of flocculants, silica suspension was stirred at a constant speed of 75 rpm for 2 min, followed by low stirring at 25 rpm for 3 min. The flocculant concentrations were varied to optimize the dosage at different pH conditions. The pH was adjusted by using 0.1 (M) HCl and 0.1 (M) NaOH solutions. After 15 min, supernatant was withdrawn and residual turbidity was measured using turbidity meter. Zeta potential of supernatant liquid, average floc size of the formed flocs were measured using Zetasizer Nano ZS (Malvern, UK).

2.4.2. Kinetics study

To determine the flocculation kinetics, 1 wt% silica suspension was taken in 1 L beaker (4 g of silica was dispersed in 400 mL of distilled water). The experiment was continued up to 5 min by constant stirring (100 rpm) of suspension after addition of flocculant. Subsequently, the flocs were allowed to settle down for predetermined time period. Finally, a fixed volume of suspension was withdrawn, filtered, dried and weighed.

2.5. Flocculation characteristics using various industrial effluents

Wastewaters from textile, paper and mine industries were characterized by their colour, suspended solids, and dissolve contaminants. These industries used to discharge their wastewaters with minimum treatment like pH neutralization or insufficient removal of colour. Thus it is essential to treat these industrial effluents properly before its discharge. g-AP has been used here to remove various toxic contaminants, as well as colour from different industrial sources. Moreover the pilot plant study of mine processwater has been focused mainly on the novel impact of environmental remediation. It has been observed from jar test experiment as well as from kinetics study that 9 ppm of flocculant concentration (g-AP) is optimized and accordingly we use 9 ppm flocculant dosage for the treatment of various industrial effluents.

2.5.1. Treatment of paper effluent

The paper wastewater was treated using 9 ppm of flocculants. After addition of flocculant, 200 mL of paper effluent was initially stirred at a speed of 75 rpm for 2 min and then at 25 rpm for 3 min. After which, it was kept in undisturbed situation for 15 min. Subsequently, the clear solution was withdrawn from the top layer and was investigated for various chemical/environmental analyses such as turbidity, total solid (TS), total dissolved solid (TDS), total suspended solid (TSS). The toxic metal ions, for instance, Zn^{2+}, Pb^{2+}, Fe^{3+} present in the effluent (before and after treatment) were analyzed using Atomic Absorption Spectrophotometer (Thermo Scientific-ICE 3000 Series AA Spectrometer).

Neat AP and FL-910 SNF were also used as flocculants for comparison.

2.5.2. Flocculation of cationic/anionic dye

Methylene blue (MB, a cationic dye) and reactive blue (RB, an anionic dye) were used as synthetic dye effluent. The flocculation characteristics were carried out at pH 4 for RB and at pH 9 for MB using different flocculants used under study. The pH was controlled by using 0.1(M) HCl and 0.1(M) NaOH solutions. At specific pH, the experiment was carried out using 25 mL, 30 mg/L of respective synthetic dye effluent. Dosage of flocculant were varied from 1 to 13 ppm. Then the mixture was stirred at 75 rpm for 3 min followed by 25 rpm for 2 min. Afterwards, the flocs were allowed to settle for 45 min and the clean supernatant was withdrawn from the top layer of solution and the colour removal was determined by UV-Visible Spectrophotometer (Shimadzu, Model: UV 1800). The result has been represented graphically using % decolourizing efficiency (% DE) vs. flocculat dosage. % DE was measured using Eq. (1)

$$\%DE = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A and A_0 are the absorbencies of the supernatant liquid after and before addition of flocculant, respectively.

2.5.3. Treatment of textile wastewater

g-AP was investigated as flocculant to realize the colour removal efficiency from real textile wastewater. The removal of dye was carried out in inherent pH of the effluent. 50 mL of textile effluent was taken and optimized flocculant concentration (i.e. 9 ppm) was