Colloid Polym Sci (2006) 284: 443–448
DOI 10.1007/s00396-005-1399-x

SHORT COMMUNICATION

Anuradha Mishra
Malvika Bajpai

Removal of sulphate and phosphate from aqueous solutions using a food grade polysaccharide as flocculant

Received: 25 February 2005
Revised: 4 May 2005
Accepted: 11 July 2005
Published online: 25 October 2005

A. Mishra (✉) · M. Bajpai
Department of Chemistry, University Institute of Engineering and Technology, CSJM University, Kanpur 208 024, India
E-mail: anuradha_mishra@rediffmail.com
Tel.: +91-512-2218330

Abstract The mucilage extracted from the seeds of Tamarindus *indica* pods, a food grade natural polysaccharide, is used as a flocculant for removal of sulphate and phosphate ions in aqueous medium. The maximum removal obtained was 73.71% for sulphate ions and 75.71% for phosphate ions after 30 min. The optimum mucilage dose was 50 mg/L for both sulphate and phosphate ions. The maximum removal was obtained at acidic pH for both the ions. A series of contact time experiments were conducted to assess the system variables such as concentrations of mucilage and ions and pH. The conductivity measurements were also done and correlated with the percent removal. This eco-friendly food grade polysaccharide was proved to be a very good flocculant for the removal of sulphate and phosphate ions.

Keywords Tamarind mucilage · Sulphate ions · Phosphate ions · Flocculation · Jar test method

Introduction

Textile industries are one of the largest consumers of water and perhaps one of the most potential polluters of aquatic environment. These industries convert natural and synthetic materials to finished products through various processes. The pollutants released from these industries include different coloring agents, sulphates, nitrates, phosphates and many heavy metals like chromium, nickel, copper and iron etc. Some of the micropollutants like sulphates and phosphates occur naturally in most water supplies and also in wastewaters. During various processes like washing, printing and bleaching, salts of phosphates and sulphates are released in the effluent. These pollutants come into contact with water and soil and, consequently, adversely affect the health of living beings and fertility of the soil [7, 17]. The presence of high sulphate and phosphate concentration in textile wastewater causes deficiency of oxygen either in the aquatic media or sewerage system. The negative impact of sulphur is due to its reduction under anaerobic conditions to sulphide, which in turn can combine with hydrogen to form hydrogen sulphide. This hydrogen sulphide can then be oxidized biologically to sulphuric acid. Sulphates and phosphates increase the solid content of water and are responsible for corrosion. Scale formation in the boilers takes place due to presence of these salts. The permissible limit for sulphate and phosphate ions in water is 150 ppm and 10 ppm according to the Indian standards.

The discharge of wastewater into environment, without proper treatment, may cause serious and long-lasting consequences. In water reuse technology, various techniques have been employed in the past [5]. Adsorption, flocculation/coagulation and biological processes are the various treatment technologies for textile wastewater. Flocculation/coagulation, using alum, ferric sulphate, lime and some synthetic organic polymers, is proved to be effective and relatively inexpensive method for textile wastewater [2] treatment. However, some studies [8] have reported that aluminium, major component of alum, may induce Alzheimer's disease. It was also reported that monomers of some synthetic organic polymers have neurotoxicity and strong carcinogenic properties [9], whereas natural flocculants, mainly polysaccharides, are safer for environment and mankind. Recently, there has been a resurgence of interest in natural flocculants/coagulants [13] for wastewater treatment in developing countries [5].

Recently, we have reported the use of some natural polymers for the treatment of various types of wastewaters [1, 10, 11]. In the present study, a brief evaluation of the effectiveness of Tamarindus mucilage as flocculant for sulphate and phosphate removal is given. The variables studied are the mucilage dose, contact time and pH.

Materials and methods

Tamarindus mucilage was extracted from the seeds of Tamarindus *indica*. The flour of the seed kernel was soaked in distilled water overnight. The thick mucilaginous liquid obtained was filtered through muslin cloth. It was then precipitated by adding three parts of isopropanol to one part of the aqueous extract. The residue was then washed with acetone two to three times to remove impurities and finally dried by keeping in oven at 40 °C for 24 h.

The mucilage solutions of different concentrations were prepared in distilled water. It is soluble in lukewarm water. The viscosity of these solutions was measured by an Ostwald viscometer. The intrinsic viscosity measured from the point of intersection was obtained after extrapolation of two plots, i.e., η_{Sp}/C versus C and ln η_{rel}/C versus C to zero concentration. Where C is the concentration of polymer in g/dL; $\eta_{Sp}/C = \eta_{rel} - 1/C$; $\eta_{rel} = \eta/\eta_o = t/t_o$, where t is the time of flow of the solvent at the time of measurement.

Barium chloride, magnesium chloride, potassium dihydrogen phosphate, acetone, methanol (S.D. Fine chemicals, India), sodium sulphate (BDH)B, sodium acetate (Sarabhai M Chemicals Ltd.), potassium nitrate (Merck) and acetic acid (Qualigens) were used in the present study. All the chemicals were of analytical grade and were used as received, without any purification. Isopropanol and buffer tablets were purchased from BDH (India) and acetone from S.D. Fine-Chem (India). The solutions were prepared in distilled water. The known concentrations of solutions of sulphate and phosphate salts were prepared in order to get optimal flocculant dose and optimal time for the treatment of wastewater. The concentrations of sulphate and phosphate were analyzed using Perkin Elmer, Lambda 40, UV–Vis spectrophotometer at wavelengths, 420 and 690 nm, so as to obtain maximum absorbance. All tests were done at room temperature (32 ± 2 °C) to eliminate any temperature effects. The pH values for the test solutions were measured by microprocessor pH meter CP931.

The percent sulphate and phosphate removal was calculated from initial (C_o) and final equilibrium (C_e) concentrations of test solutions as follows [15]:

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \ldots \quad (1)$$

Flocculation experiments

Jar test is the most widely used method for evaluating and optimizing the flocculation/coagulation processes [12]. This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. The different concentrations chosen for jar experiments were in the range of 150–500 mg/L for sulphate ions and in the range of 10–100 mg/L for phosphate ions. Three hundred millilitres of flocculant-ions solutions (sulphate and phosphate ions solution were prepared separately from their salts) were agitated in a flocculator at 100 rpm for 1 min and then 30 rpm was quickly established for 10 min. The apparatus allowed six beakers containing simulated wastewater to be agitated simultaneously. After slow mixing, the beakers were carefully removed from the flocculator and were placed in a safe place for sedimentation phase to take place. The duration of sedimentation was kept constant at 10 min. At definite intervals, the supernatant solution was taken out, decanted and centrifuged. It was then analyzed spectrophotometrically using standard methods [14, 16]. Several contact time experiments were undertaken to assess the effect of system variables.

Result and discussion

Characterization

Tamarindus *indica* mucilage is a natural polysaccharide composed of D-galactose, D-glucose and D-xylose. The intrinsic viscosity of Tamarindus mucilage was found to be 3.20 dL/g.

Flocculation studies

Effect of mucilage dose

The effect of mucilage dose on percent removal of sulphate and phosphate ions from their individual solution are shown in Fig. 1. It is apparent that with increase in mucilage dose up to a certain level, the percent removal of sulphate and phosphate ions increases and then a decreasing trend in removal was observed with further increase in dose level. The most effective dose of floc-

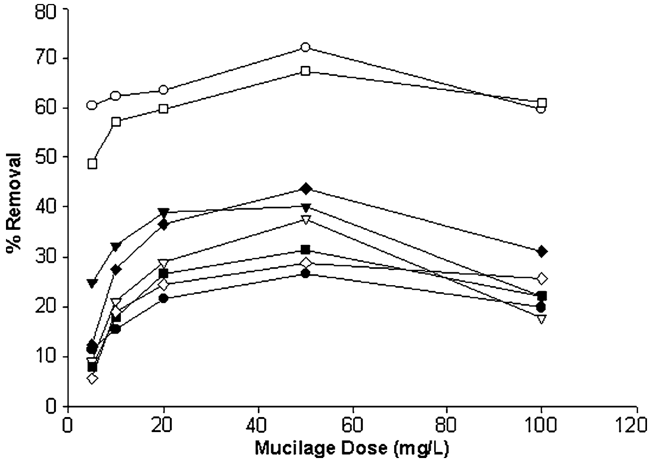

Fig. 1 Percent removal versus mucilage dose. (*filled circle*) 100 mg/L, (*open circle*) 150 mg/L, (*filled inverted triangle*) 200 mg/L, (*open inverted triangle*) 500 mg/L of sulphate ions, (*filled square*) 5 mg/L, (*open square*) 10 mg/l, (*open diamond*) 20 mg/L, (*filled diamond*) 50 mg/L of phosphate ions. Contact time of mucilage and sulphate ions = 30 min; pH of the sulphate ion solution = 5.23–8.27; contact time of mucilage and phosphate ions = 60 min; pH of the phosphate ion solution = 6.28–9.61

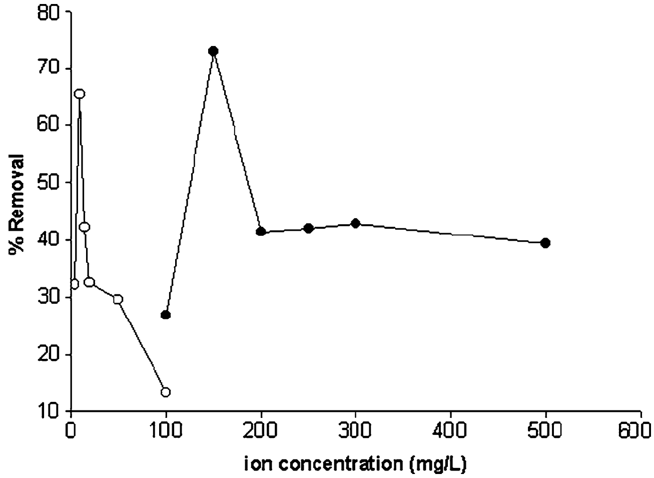

Fig. 2 Effect of initial concentration of ions on percent removal of sulphate ions (*filled circle*) and phosphate ions (*open circle*). Mucilage dose = 50 mg/L; contact time of mucilage and sulphate ions = 30 min; contact time of mucilage and phosphate ions = 60 - min

culant was found to be 50 mg/L for both sulphate and phosphate ions at which the maximum removal was seen.

In the present experimental conditions, it is very likely that the polymer bridging plays a large part in the flocculation process, and the higher the dosage of mucilage, the more likely is aggregation between colliding particles. This trend (increasing and then decreasing trend) in percent removal is because of the fact that the optimum amount of mucilage in the suspension causes larger amount of sulphate and phosphate ions particle to aggregate and settle. However, an over optimum amount of mucilage in sulphate and phosphate ions solution would cause the aggregated particle to redisperse and would also disturb particle settling [3]. This behaviour could also be explained on the basis of a great degree of increase in the repulsive energy between the mucilage and sulphate and phosphate ions solution, which causes hindrance in floc formation.

A proper justification for same optimal polymer dose for both the ions might be attributed only to the fact that there is direct stoichiometric relationship between optimum polymer dosage and colloid concentration, and the restabilization due to overdosing of flocculant or colloidal particles can occur.

Effect of sulphate and phosphate ions concentration on percent removal

The effect of sulphate and phosphate ion concentration on percent removal is depicted in Fig. 2. It showed that on varying the concentration of the sulphate ions from 100 to 150 mg/L, the percent removal increases from 26.9 to 72.8% and on further increasing the concentration up to 500 mg/L, percent removal decreases from 72.8 to 39.25%. On varying the phosphate ions concentration from 5 to 10 mg/L, the percent removal increases from 32.1 to 65.4% and on further increasing the concentration up to 100 mg/L, the % removal decreases from 65.4 to 19.8%. Therefore, the optimal sulphate ion concentration was 150 and 10 mg/L for phosphate ion.

The reason for the above observation may be attributed to the larger increase in the denominator (C_o) value in comparison to that of the ($C_o - C_e$) value in Eq. 1. The flocculating capacity of the mucilage probably became exhausted beyond 150 and 10 mg/L concentration of sulphate and phosphate ions, respectively. The explanation for this observation is based on a particle-polymer-particle complex formation in which polymer serves as a bridge. To be effective in destabilization, a polymer molecule must contain chemical groups, which can interact with sites on the surface of the colloidal particle. When a polymer molecule comes into contact with a colloidal particle, some of these groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution. If a second particle with some vacant adsorption sites contacts these extended segments, attachment can occur. A particle-polymer-particle complex is thus formed in which polymer serves as a bridge. If a second particle is not available in time, the extended segments may eventually adsorb on other sites on the original particle, so that the polymer is no longer capable of serving as a bridge.

Effect of contact time on percent removal

The effect of percent removal of the sulphate and phosphate ions, with contact time using the optimal mucilage dose, i.e., 50 mg/L, is shown in Fig. 3. The maximum removal of the sulphate and phosphate ions from their individual solutions was found to be after 30 min and 60 min, respectively. However, it took only 30 min for maximum removal (Table 1) of both the ions when a solution containing both sulphate and phosphate was studied. Since sulphate salt formed big flocs in shorter time as compared to those of phosphate salt and these flocs probably gave an additional surface for adsorption of phosphate ions, therefore, the reduction in time for the removal of phosphate in the presence of sulphate ions was observed.

As seen from Fig. 3, equilibrium with an initial decrease in percent removal is evident after certain duration. This equilibrium is attained in 30 min and 60 min for sulphate and phosphate ions, respectively, which is irrespective of their initial concentrations (Table 2). A sloped curve indicates the flocculation capacity of the mucilage. The plot visualized three distinct phases: the first phase (initial steep slope) indicated the interaction of inorganic anions concentration molecules with flocculant, which caused destabilization of the particles in suspensions, and they began to flocculate. The second phase of the plot showed slight decrease in percent removal of the anions; this may be due to destabilization of the aggregated particles [1]. The third phase of plot indicated attainment of stability by the flocs.

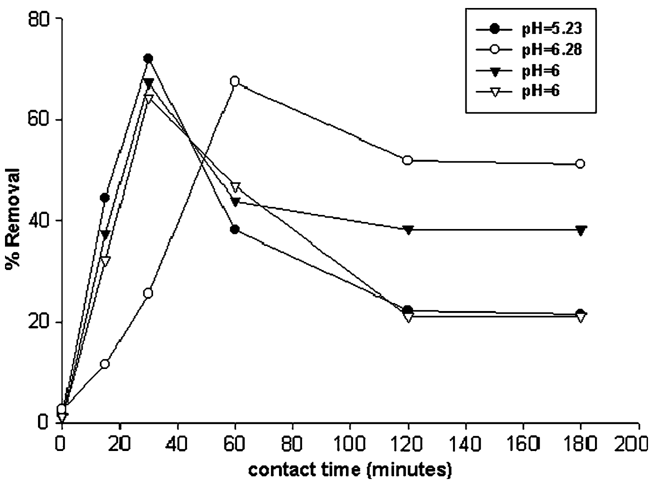

Fig. 3 Effect of percent removal of sulphate (*filled circle*) and phosphate (*open circle*) in individual solution, and sulphate (*filled inverted triangle*) and phosphate (*open inverted triangle*) in joint presence of both the ions with contact time. Mucilage dose = 50 mg/L

Effect of pH on the sulphate and phosphate ions' removal

Figure 4 shows the removal of sulphate and phosphate ions as a function of pH. The maximum percent removal was observed at acidic pH for both sulphate and phosphate ions. The maximum removal observed for sulphate ions was ~78.6% and for phosphate ions, it was 72.4%, with mucilage dose of 50 mg/L in each case. The maximum removals were 73.71% and 75.71% for sulphate and phosphate, respectively, in joint presence of both ions. This observation showed that the percent removal remained almost same in both the cases, i.e., the individual solutions and mixed solution. The removal at acidic pH could be justified on the basis of the fact that acidic species adsorb better at low pH since negatively charged particles start getting neutralized at low pH values [4].

The conductivity values were also related to the flocculant dose and the concentrations of sulphate and phosphate ions in the solution. It was observed that the conductivity increases with increase in percent removal in each case. The decrease in conductivity value with an increase in pH indicates a high degree of suspension stability in the alkaline pH range and less in the acidic range. This means that at acidic pH, destabilization was achieved and the suspension began to flocculate.

Conclusion

From the present set of experiments, Flocculation, using Tamarindus mucilage for sulphate and phosphate removal, was shown to be a simple and efficient treatment from an economic and technical point of view. The

Table 1 Percent removal of SO_4^{2} and PO_4^{3-} ions in joint presence of both the ions

S. no.	Anion concentration (mg/L)	pH	Percent removal within					
			5 min	10 min	15 min	30 min	60 min	120 min
1	(SO_4^{2-})150	6	2	27.85	37.38	67.32	43.91	38.24
2	(PO_4^{3-})10	6	17.89	29.96	41.17	75.71	60.19	31.04
3	(SO_4^{2-})150	4	22.32	37.45	42.21	73.71	62.43	34.16
4	(PO_4^{3-})10	4	25.61	35.52	41.17	75.71	60.19	31.04

Table 2 Percent removal of SO_4^2 and PO_4^{3-} ions on varying their concentration in their individual solution

S. no.	pH	Anion concentration (mg/L)	Percent removal within					
			0 min	5 min	10 min	15 min.	30 min	60 min
1	Ranges between 5.23 and 7.14	(SO_4^{2-})100	1.25	12.25	26.6	26.12	26.10	25.97
2		(SO_4^{2-})150	1.6	44.6	72.1	38.1	22.3	21.5
3		(SO_4^{2-})200	1.69	19.65	40.01	38.82	38.46	38.20
4		(SO_4^{2-})300	1.53	15.62	39.7	35.53	34.87	34.87
5		(SO_4^{2-})500	1.05	29.6	37.6	36.8	36.1	35.9
6	Ranges between 6.66 and 11.42	(PO_4^{3-})5	1.04	12.6	19.85	31.4	29.8	29.79
7		(PO_4^{3-})10	2.7	11.53	25.6	67.4	51.8	51.1
8		(PO_4^{3-})20	1.26	7.85	21.65	43.6	42.25	41.96
9		(PO_4^{3-})50	1.48	3.56	11.6	28.8	27.9	27.8
10		(PO_4^{3-})100	1.59	4.82	10.3	15.6	15.6	15.4

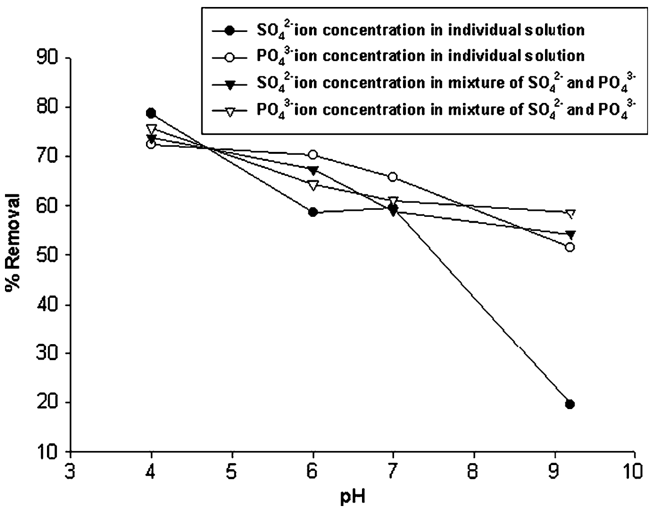

Fig. 4 Influence of pH variation on percent removal of sulphate and phosphate. Sulphate ion concentration = 150 mg/L; phosphate ion concentration = 10 mg/L

maximum removal of the sulphate and phosphate ions was 73.71 and 75.71% after 30 min. The optimum mucilage dose was 50 mg/L in each case. The acidic pH seems to be the most effective pH value for the removal of both sulphate and phosphate. The bridging mechanism was proposed for flocculation of anions by this mucilage. It was concluded that the use of such natural polymers as flocculants for the removal of anions from industrial wastewater might be preferred because of their non-toxic nature and low capital cost as well as the lower operating costs when compared to other technologies. A site-specific preliminary bench test and then an appropriate pilot study to ensure long-term performance reliability and to establish realistic scale-up costs are recommended to evaluate the full potential of the Tamarindus mucilage as flocculant.

Acknowledgements The authors are grateful to University Grants Commission, New Delhi for financial support of this study [Project No. F. 12-133 / 2001 (SR –1)].

References

1. Agarwal M, Rajani S, Rai JSP, Mishra A (2003) Utilization of biodegradable okra gum for the treatment of tannery effluent. Int J Polym Mater 52:1049–1057
2. Boon HT, Tjoon TT, Mohd Omar AK (2000) Removal of dye wastes by magnesium chloride. Water Res 34:597–601
3. Chan WC, Chiang CY (1995) Flocculation of clay suspension with water insoluble grafted acrylamide/sodium allylsulphonated copolymer powder. Appl Polym Sci 58:1721–1726
4. Cooney DO (1999) Adsorption design for wastewater treatment. CRC Press LLC, Florida, p 33
5. Grau P (1991) Textile Industry Wastewaters Treatment. Water Technol Environ Eng 24:97–103
6. Gupta GS, Prasad G, Singh VN (1990) Removal of chrome dye from aqueous solutions by mixed adsorbents:fly ash and coal. Water Res 24:45–50
7. Khan AU, Ajmal M (1985) Studies of the dissociation of oxide surfaces at the liquid-solid interface. Can J Chem 44:1663–1668
8. Martyn CN, Barker DJP, Osmond C, Harris EC, Edward JA, Lacey RF (1989) Geographical relation between alzheimer's disease and aluminium in drinking water. Lancet 1:59–62
9. Mccollister DD, Oyen E, Rowe VK (1964) Toxicology of acrylamide. Toxicol Appl Pharmacol 6:172–181
10. Mishra A, Bajpai M (2005) Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide. J Hazard Mater B118:213–217
11. Mishra A, Yadav A, Agarwal M, Bajpai M (2004) Fenugreek Mucilage for Solid Removal from Tannery Effluent. React Funct Polym 59(1):99–104
12. Ndabigengesere A, Narasiah KS (1998) Quality of water treated by coagulation using moringa oleifera seeds. Water Res 32:781–791

13. Okuda T, Baes AU, Nishijima W, Okada M (1999) improvement of extraction method of coagulation active components from moringa oleifera seed. Water Res 33(15):3373–3378
14. Rossum JR, Villarruz P (1961) Suggested methods for determination of sulphate in water. J Am Water Works Assoc 53:873
15. Samantaroy S, Mohanty AK, Misra A (1997) Removal of hexavalent chromium by kendu fruit gum dust. J Appl Polym Sci 66:1485–1494
16. Sheen RT, Kahler HS, Ross EM (1935) turbidimetric determination of sulphate in water. Ind Eng Chem Anal Ed 7:262
17. Walsh GE, Bahner LH, Horning WB (1980) Toxicity of textile mill effluents to fresh water and estuarine algae crustaceans and fishes. Environ Pollut Ser A 21:169–173