

Trigonella Foenum-Graecum Mucilage: An Adsorbent for Removal of Sulphate Ions

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Abstract: *The mucilage extracted from the seeds of Trigonella foenum-graecum, a food grade natural polysaccharide, is used as an adsorbent for removal of sulphate ions in aqueous medium. The maximum removal obtained was 87.80% after 60 minutes. The optimum mucilage dose was 50mg/L. The maximum removal was obtained at acidic pH. A series of contact time experiments were conducted to assess the system variables such as concentrations of mucilage and ions and pH. This ecofriendly food grade polysaccharide was proved to be a very good adsorbent for the removal of sulphate ions.*

Keywords: *mucilage, trigonella, polysaccharide, adsorbent*

1. INTRODUCTION

Sulfate occurs naturally in groundwater. Sulfate ions present in water in high concentrations may cause temporary and acute effects on humans and animals, including diarrhea. The United States Environmental Protection Agency (U.S. EPA) has proposed a maximum allowable concentration of 500 mg/L for sulfate in drinking water in order to avoid any health concern regarding human consumption (Ashref et al ¹). Different treatment technologies have been investigated for sulfate removal. Following technologies for the removal of sulfate from drinking water include ion exchange, nanofiltration and reverse osmosis (Marhaba and Washington ²)

A study conducted by Rao and Sridharan ³ on the adsorption of sulfate by kaolinite found that sulfate was adsorbed at positive and neutral sites with the displacement of OH₂ and OH- groups.

Industrial waste waters contain high concentration of sulfates which should be removed before discharge to receiving waters or municipal sewerage. Several processes are currently employed for sulphate removal and acid water neutralization, e.g. biological removal by Maree et al ⁴ and chemical processes (limestone, Smit ⁵) reverse osmosis and electrodialysis).

1.1. Chemical Method

The integrated limestone/lime treatment process can be used for neutralization of acid water and partial sulphate removal to below the saturation level of gypsum, i.e. 1 200 mg/l. (Maree and Duplessis ⁷)

The barium sulphide process removes sulphate from mine water by precipitating barium sulphate with BaS., The process has a water recovery of 70 % for a 25 ml / d.(Bosman et al ⁸)

Nilsen et al ⁹ described a liquid emulsion membrane process for removing sulfate anions from waste water..

Tait et al ¹⁰ described the use of precipitation for low-cost sulfate removal, in highly contaminated streams (>1 gS L(-1)).Wastewaters from the production of edible oils contain high concentration of phosphates, sulphates and organic compounds. Surprisingly the liquid associated with the floated sludge contained definitely lower concentrations of sulfates, only of about 300 mg/l. (Przywara L ¹¹).

Claudia et al ¹² described the feasibility of sulfate removal from complex laboratory wastewaters using barium and calcium precipitation. Mishra and Bajpayi ¹³ studied the mucilage extracted from the seeds of *Tamarindus indica* pods

1.2. Reverse Osmosis (RO) Method

Reverse osmosis (RO) is a water treatment system that removes most dissolved substances, such as sulfate, from water by forcing the water through a cellophane-like plastic sheet known as a "semipermeable membrane." It can typically remove between 93 and 99 percent of the sulfate in drinking water depending on the type of unit.

1.3. Ion Exchange Method

Ion Exchange is the most common method of removing large quantities of sulfate from water for commercial, livestock, and public supplies, but is not commonly used for individual household water treatment. It is a process where one element or chemical is switched for another.

1.4. Biological Method

Biological process under anaerobic conditions convert sulfates into sulfides which in addition can be removed (precipitated) as ferrous sulfide (Jong T. and Parry D.L ¹⁴). Elke et al ¹⁵ studied a long-term study process of biological sulfate reduction in anaerobic two-stage pilot plants treating tannery wastewater with the objective to reduce most of the sulfate in the first stage Chen and Horan ¹⁶ investigated a two-stage anaerobic/aerobic biological process was for its ability to remove sulphate from a pulp and paper mill effluent Rose et al ¹⁷ described a process for treating sulphate-containing waste water comprises introducing feedstock comprising sulphate-containing waste water, into a pond. Feng et al ¹⁸ demonstrate the possibility of electricity generation in a microbial fuel cell (MFC) with concomitant sulfate removal by employing the sulfate-reducing bacterium *Desulfovibrio desulfuricans*. This approach is based on an in situ anodioxidative depletion of sulfide produced by *D. desulfuricans*

1.5. Adsorption

Adsorption is one of the most popular methods for the removal of heavy metals from the wastewater inexpensive method for textile wastewater (Boon et al ²⁰) treatment.

1.6. Modified Organic Adsorbents

Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Among these, the use of adsorbents containing polysaccharides has been investigated as a replacement for current conventional methods of removing pollutants from solution.

1.7. Polysaccharides

Polysaccharides, stereoregular polymers of monosaccharides (sugars), are unique raw materials in that they are: very abundant natural polymers (they are referred to as biopolymers); inexpensive (low-cost polymers); widely available in many countries; renewable resources; stable and hydrophilic biopolymers; and modifiable polymers. They also have biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, polyfunctionality, high chemical reactivity, chirality, chelation and adsorption capacities.

By neutralizing the effluent and removing the sulphate acid mine drainage may be remediated currently a variety of sulphate removal technology are available. These include:

- Deasilation process, such as reverse osmosis and ion exchange (Dill et al ²¹)
- Chemical method, using barium ion such as barium hydroxide or barium chlorides (Maree and Strydom ²²)
- Biological removal of sulphate, using sulphate reducing bacteria (Dill et al ²¹) various experiment using different bioreactor setups and different carbon sources have been studied for potential use I the biological removal of sulphate by SRB (Tuttle et al ²³; Maree and Strydom ²²; Du Preez et al ²⁴; Van Houten et al ²⁵)

1.8. The Need To Remove Sulfate Ions from Water

Historically, sulfate in water has not generally been subject to regulation. However, with the increasing realization that global water resources are limited and are declining as the population grows and consumption increases, stricter regulations of water quality are being imposed to allow for its re-use or its safe disposal into the environment. For sulfate this has meant the introduction of water quality regulations in a number of jurisdictions worldwide to respond to the need to protect the health of humans, domestic animals, agriculture, and the fauna and flora in the environment. Sulfate is not toxic to humans except at very high concentrations, however, it does increase total dissolved solids (TDS), or salinity, impart taste and odor to drinking water at lower concentrations and can cause digestive disorders at concentrations that are typically found downstream of mining and other industrial operations. For domestic and wild animals, drinking water containing sulfate can cause similar ailments and possible reproductive disorders. In addition to environmental concerns, sulfate, particularly as calcium sulfate, can cause problems in process waters due to scaling of boilers, heat exchangers, agitated tanks, pumps, pipelines and other process equipment. The fundamental requirement of any process to remove sulfate from water is that it has the capability to meet the regulatory limits imposed. Traditionally, dissolved metals and the associated acidity in wastewater have been removed by precipitation and neutralization by adding lime, normally as calcium hydroxide. Reaction with lime removes metals by precipitation as hydroxides and also causes the removal of sulfate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

2. EXPERIMENTAL

2.1. Description of Seed Gum



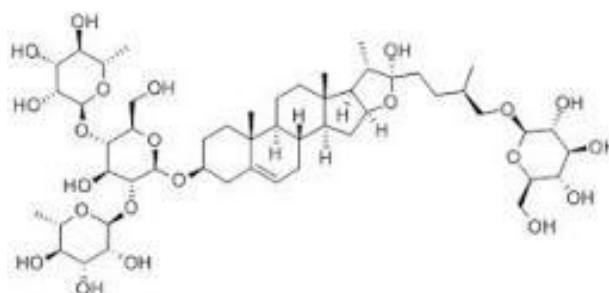
Fig 1. Fenugreek (Leaves and seeds)

Botanical Name - *Trigonella foenum-graecum*

Family - Leguminosae

Fenugreek seeds are a rich source of the polysaccharide galactomannan. They are also a source of saponins such as diosgenin, yamogenin, gitogenin, tigogenin, and neotigogens. Other bioactive constituents of fenugreek include mucilage, volatile oils, and alkaloids such as choline and trigonelline. Galactomannans are reserve polysaccharides consisting mainly of the monosaccharides mannose and galactose units. The mannose-elements form a linear chain consisting of (1→4)-β-D-mannopyranosyl residues, with (1→6) linked α-D-galactopyranosyl residues as side chain at varying distances,

Chemical structure of fenugreek mucilage



2.2. Techniques and Equipments Used

pH Measurements

Model Make: Systronics pH Meter CP 931

The pH of the aqueous solutions of polymer and of wastewater sample was measured by microprocessor pH meter CP 931.

2.3. Ultraviolet and Visible Spectroscopy

Isolation and Purification of Natural Polysaccharide

Fenugreek mucilage was extracted from powdered seeds of *Trigonella foenum-graecum*. The seed powdered and distilled water was added and slurry was prepared. The resulting thin clear solution was kept overnight so that most of the proteins and fibers settled out. The mucilaginous extract was filtered through muslin cloth. It was precipitated from the extract by addition of EtOH. The crude mucilage was collected, washed with acetone and dried by keeping in oven at 40°C for 24 hours.

2.4. Purification

The mucilage was deproteinized by Sodium complexing .5% (w/v) aqueous solution of crude mucilage was prepared by continuous stirring with water for 12h at 60°C and precipitating with saturated sodium hydroxide solution. The complex was separated by centrifugation and taken in 1M acetic acid stirred for 8h, centrifuged and precipitated with methanol. It was washed with 70, 80, 90 and 95% methanol. The precipitate was finally dried by keeping in oven at 40°C for 24 hours.

2.5. Flocculation Studies

The flocculation efficiency of mucilage and its acrylamide-grafted copolymers with simulated and real textile effluents was determined at room temperature. The effects of varying concentrations of flocculants and the critical pollutants like various dyes, inorganic ions and chromium ions; pH and contact time on flocculation capacity of the flocculants were also studied.

2.6. Method of Flocculation

Flocculation studies were conducted by standard jar test method (Huck et. Al²⁶).

The critical pollutant concentration in treated and untreated wastewater solutions was measured using UV-VIS spectrophotometer. The equation used to calculate the percent removal in the treatment experiments was-

$$\% \text{ Removal} = \frac{C_0}{C_0 - C} \times 100 \quad (6)$$

Where

C_0 = Concentration of untreated sample

C = Concentration of treated sample

2.7. Estimation of Sulphate

Sulphate ions were determined by colorimetric method (Standard Methods, 1995). 0.05ml of phenolphthalein indicator is added to the 100 ml of test sample, it turns pink. Strong acid solution is added drop wise to discharge the color. Then 0.5 ml of stannous chloride solution is added with continuous shaking. Sample is analyzed after 10±2 min. by UV-VIS Spectrophotometer at 420 nm and compared with the calibration curve.

2.8. Affecting Adsorption

Variables studied included concentration of adsorbent, concentrations of sulphate ions, contact time and pH.

2.9. Concentration of Pollutant Ions

The effect of variation of sulphate ions concentration on percent removal was studied. The pollutant ions concentration in simulated samples (made in distilled water) was varied in the range given in Table-1. The permissible limits in the effluent samples are also given in Table-1

Table 1.

Critical Pollutant	Permissible Limit	Concentrations Studied
Sulphate	150 mg/L	500-5000 mg/L

2.10. Contact Time

The effect of contact time on flocculation efficiency was studied by measuring phosphate ions concentration in simulated samples at varying time intervals.

pH

Adsorption efficiency was also studied at varying pH values (4.0, 6.0, 7.0 and 9.2). The pH of the solution was maintained by addition of buffer solution of required pH in the treating samples.

3. RESULTS AND DISCUSSION

3.1. Infra Red Spectroscopy

Infra red spectroscopy of Graft Copolymer

The FTIR spectra of pure Fen. The FTIR spectra of purified fenugreek shows characteristic peaks of -OH between 3509-3150 cm^{-1} , ether linkage at 1455-1400 cm^{-1} , -CH stretching between 2923-2854 cm^{-1} , -CO stretching at 1018 cm^{-1} and -CH₃ at 2923 cm^{-1} .

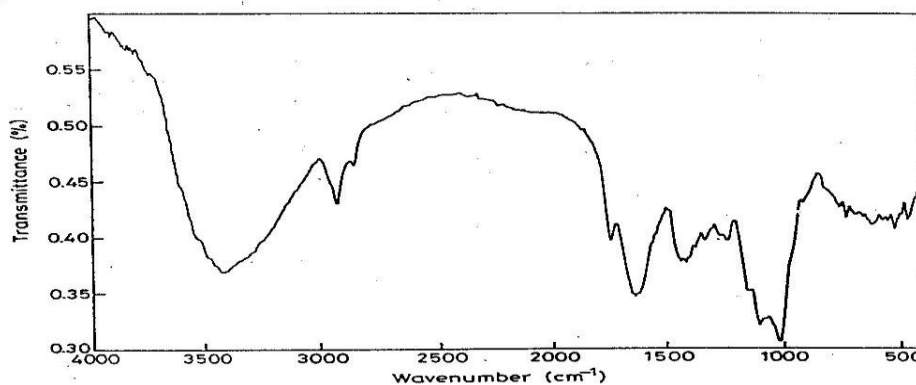


Fig 2. IR spectra of Fenugreek mucila

3.2. Removal of Sulphate Ions

Effect of fucilage dose

Figure .1 shows the effect of variation in the amount of adsorbent dose on the percent removal of sulphate ions. It was observed that within the range studied, the percent removal increased with an increase in adsorbent dose up to 50 mg/L. The related data are presented in Table 2. The increase in the percent removal with an increase in the amount of mucilage might be attributed to the availability of increased surface area or active sites for the adsorption. An increase in mucilage concentration beyond optimum dose, however, showed the decrease in percent removal.

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 % removal is because of the fact that the optimum amount of mucilage in the suspension causes larger amount of phosphate ions particle to aggregate and settle. However, an over optimum amount of mucilage in phosphate ions solution would cause the aggregated particle to redisperse and would also disturb particle settling (Chan and Chiang²⁷; Mishra and Bajpai²⁸).

Table 2.

Mucilage dose (ppm)	% removal
2	10.20
5	17.30
10	33.40
20	45.50
50	100
100	58.6

3.3. Effect of Concentration of Sulphate Ions

The effect of sulphate ions concentration on percent removal is depicted in Figure .2. showed that on varying the concentration of sulphate ions concentration from 1000 mg/L to 3000 mg/L, the percent removal increased from 49.10 % to 76.92 % and on further increase in the concentration up to 5000 mg/L, the percent removal decreased from 76.92 % to 60.20 %. Therefore, the optimal sulphate ions concentration was 3000 mg/L. The related data are presented in Table3.

The reason for the above observation may be attributed to the larger increase in the denominator (Co) value in comparison to that of the (Co)Ce value in Eq. 1. The flocculating capacity of the mucilage probably became exhausted beyond 150 and 10 mg/L concentration of sulphate 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 (Mishra and Bajpai²⁹).

Table 3.

Sulphate concentration (ppm)	% Removal
1000	49.10
2000	66.66
3000	76.92
4000	72.92
5000	60.20

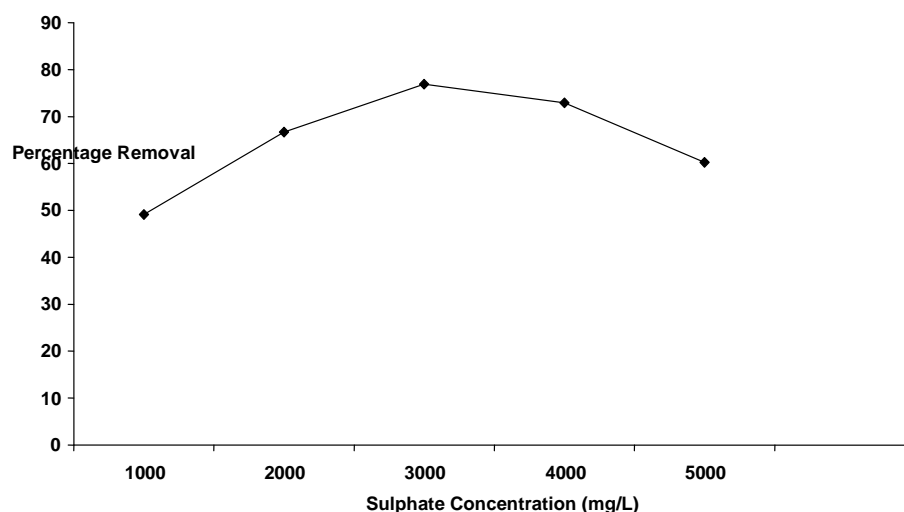


Fig 3. Sulphate Ion Concentration

3.4. Effect of Contact Time

The effect of percent removal of the anions with contact time is shown in figure .3. The maximum removal of the phosphate ions was found to be after 60 minutes. After this time percent removal and became constant. Hence, equilibrium is attained in 60 minutes for sulphate ions solutions, which is irrespective of their initial concentrations (Gupta et al ³⁰). The related data are presented in **Table 4**

Table 4.

Sulphate concentration (mg/g)	5 minute	15 minute	30 minute	60 minute	90 minute
1000	26.66	40.10	47.36	49.10	35.30
2000	36.84	42.63	52.72	66.66	50.00
3000	54.54	69.23	72.27	76.92	54.30
4000	46.12	63.63	69.23	72.92	37.25
5000	29.50	50.00	55.00	60.20	28.15

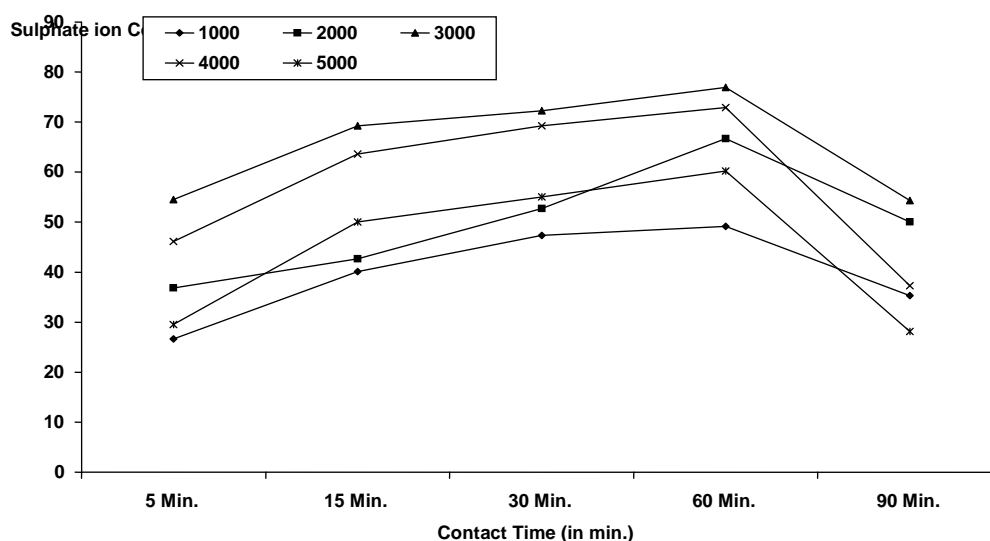


Fig. 4. Contact time variation

3.5. Effect of pH

Figure5. shows the removal of sulphate ions as a function of pH. The maximum percent removal was observed at acidic pH. The maximum removal observed 87.80% The related data are presented in **Table 5**

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 (Cooney ³¹; Mishra and Bajpai ³²).

Table 5.

pH	% removal	Time(min.)	Polymer dose (ppm)	Sulphate concentration(mg/g)
4	87.80	60	50	3000
7	76.20	60	50	3000
9.2	21.76	60	50	3000

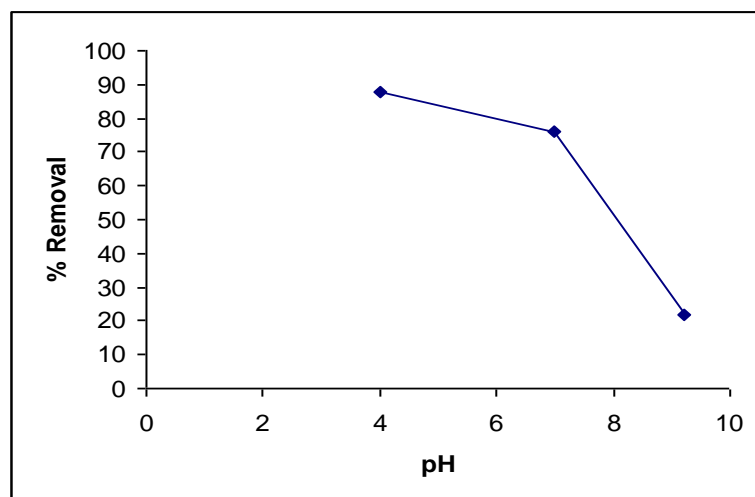


Fig 5. Effect of pH on percent removal

4. CONCLUSION

Fenugreek mucilage is reported as a flocculant for sulphate removal very first time. It was proved to be a very effective flocculant which is capable of removing almost 89% of sulphate ions from simulated sample. The optimal dose was found to be 50mg/l and the maximum removal was seen within 60 minutes of contact time. The suitable pH range for treatment was acidic. The use of such food-grade polysaccharides as flocculants could prove very beneficial because of their nontoxicity, their availability in abundance and their biodegradability. Their use at a commercial level will be a landmark in the ecologically friendly treatment of sulphate containing waste water.

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