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Performance evaluation of polysaccharides eluated from *Cyamopsis tetragonolobus* (guar gum), as a natural coagulant, in the treatment of paint industry effluent

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ABSTRACT

The performance of *Cyamopsis tetragonolobus* (guar gum) as a natural coagulant was examined in the treatment of paint industry effluent (PIE). The treatment was performed in the six stirrer arrangement jar test apparatus with base floc illuminator. The efficacy of the coagulant was confirmed through color and turbidity removal. The operational variables are eluent type (deionized water, NaCl, KCl), eluent concentration (1–5 N), coagulant dose (1–6 g), Coagulant-eluate volume (20–120 mL), initial pH (6–10) and initial effluent concentration (3,100–7,693 mg/L). From the results of this study, the optimized conditions to treat a litre of PIE was observed as 100 mL of coagulant-eluate extracted using 1 N KCl and 5 g of guar gum at its actual pH. The results revealed that the *Cyamopsis tetragonolobus* confirmed its coagulant ability in the treatment of PIE and it could act as better replacement for chemical coagulants.

Keywords: Paint industry effluent; *Cyamopsis tetragonolobus*; Coagulation; Eluate

1. Introduction

Rapid industrialization and advances in infrastructure such as transportation, energy and communication, have given further fillip to the expansion of the paint industry during the last decade [1]. The boom in the construction business aided by easy availability of housing loans is the prime driving force for the growth of the decorative paint segment. The industrial paints sector is witnessing a 50% increase in revenue, mainly due to a 10% rise in the manufacture of automobiles [2].The Indian paint industry produces around 940 million litres of paint and is valued at approximately USD 2 billion. At present, India has more than 20,000 outlets in operation, which is probably the highest for any country. 30% of the paint industry's revenue is derived from sale of industrial paints [3].

Environmental pollution is a phenomenon which is synonymous with the process of industrialization. Paints are basically chemicals that are a mixture of pigment, binder, solvent and additives. Paint can be conveniently classified based on the type of primary solvent present in them. This also determines the procedure for waste reproduction and disposal. The major constituents of the effluent generated by the paint industry are sourced from the cleaning of associated equipment and various other unit operations [4]. In the generated wastewater 80% is from cleaning of mixers, reactors, blenders, packing machines and floors [5] and not from the manufacturing process itself. Effluents from the paint industry contain highly toxic and organic bio-refractory compounds accounting for COD, BOD and TOC, which endanger aquatic life and wildlife and contaminate the food chain. Legal restrictions in organized industrial zones make it mandatory for the effluent to be treated suitably before being discharged into the environment, in this way promoting environmental conservation [6]. The treated wastewater can be effectively,

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recycled and reused within the plant as a coolant, diluant or a component of low cost paint and for effective water management.

Researchers have reported the treatment of PIWW by various methods such as physico–chemical treatment [7], bio-oxidation [8], biological treatment [9], active sludge treatment [10], microfiltration [11], coagulation–flocculation processes [12], Fenton oxidation [13], adsorption [14], electrochemical oxidation [15] and electro-coagulation [6]. Of all the listed methods of wastewater treatment, the process of coagulation–flocculation, dating back to history, has attracted considerable attention for its high removal efficiency. Its application includes removal of dissolved chemical compounds and turbidity from wastewater through the addition of conventional chemical coagulants. Many coagulants such as alum, ferric chloride, polyaluminium chloride (PAC) and calcium carbonate have been used for removing pollutants from wastewater.

By scanning through the literature it was noticed that the better way to treat the wastewater from paint industry is coagulation [4]. But the drawbacks of using chemical coagulants are high operation costs, large sludge volume and risk of health disorders [16] and so on. To overcome these problems, the efficacy of alternatives such as natural, plant-based or animal-based coagulants is being studied by researchers. The advantages of natural coagulants are as follows: the material is eco-rich, cost effective, highly biodegradable and unlikely to alter the pH of treated water, results in toxin-free treated water and produces low sludge volume. In this age of climate change, widespread environmental degradation and depletion of natural resources, the advent of plant/animal based coagulants for water and wastewater treatment is a welcome initiative in global sustenance [17].

Environmentalists have identified several plant types like *Moringa oleifera*, *Stryconus potatorum*, *Cactus* species, *Phaseolus vulgaris*, surjana seed, maize seed, tannin, gum arabic, *Prosopis juliflora* and *Ipomoea dasysperma* seed gum, as coagulants [18]. Researchers have proved the treatability of the paint industry wastewater, using plant based coagulants *Strychnos potatorum*, *Cactus opuntia* and animal based like *Portunus sanguinolentus* (crab) shells [19–21].

In recent days researchers are testing guar gum as a natural coagulant in the potable water treatment [22,23], removal of COD from wastewater [24] and in the treatment of tannery wastewater [25]. An attempt has been made in the present study to evaluate the performance of the *C. tetragonolobus* (guar gum), a plant based coagulant for the treatment of water based PIE.

2. Materials and methods

2.1. Paint industry effluent

All the chemicals used in the experiments were of analytical grade. Paint industry effluent (PIE) was made by blending different proportions of white primer and acrylic-based blue colorant (5% (v/v)) [15]. Five different samples were produced and named as sample numbers 1–5 (Table 1). The physical–chemical properties of the simulated PIE (sample 5), which resembled as the real effluent from paint industry, are listed in Table 2.

Table 1
Concentration of simulated water based PIE (made upto 1,000 mL)

Sample number	White primer (mL)	Blue colorant (mL)	Initial COD (mg/L)
1	48	2	3,100
2	46	4	4,224
3	44	6	5,650
4	42	8	6,258
5	40	10	7,693

Table 2
Physico-chemical characteristics of the simulated water based PIE (Sample number 5)

Parameters	Concentration (except for pH, color and turbidity)
pH at 25°C	7.8 ± 0.2
Color, absorbance in nm	Blue, 3.862
Total dissolved solids, mg/L	304
Total suspended solids, mg/L	6,880
Oil and grease, mg/L	19
Chloride as Cl, mg/L	68
Chemical oxygen demand (COD), mg/L	7,693
Sulfate as SO_4, mg/L	24
Biochemical oxygen demand, mg/L (3 d incubated at 27°C)	2,648
Iron as Fe, mg/L	0.05
Turbidity, NTU	2,693

2.2. Coagulant

Cyamopsis tetragonolobus (guar gum), seeds were purchased from seed shop from Pudukottai, Tamil Nadu, India. They were crushed, powdered and sieved through a 0.5 mm sieve. To extract the active polysaccharides components from *C. tetragonolobus*, the known amount of this powder was suspended in 100 mL of solvent named as eluent. The suspension was stirred for 15 min to extract the active compounds, which are responsible for coagulation. The solution was then allowed to settle for 15 min. The supernatant liquid, known as eluate, was used as a coagulant for further studies.

2.3. Experimental setup

To execute the treatment process, known volume of *C. tetragonolobus* eluate was added in a litre of PIE. The jar test apparatus (Deep Vision, India) with six stirrer arrangement, and base floc illuminator was used for the coagulation study, and agitated at a rapid mixing of 200 rpm for 2 min and slow mixing at 80 rpm for 2 min, followed by 60 min of settling span. After this, 50 mL of treated sample was collected to measure the color and turbidity. The experimental procedure was repeated to study the effect of operational variables viz., (deionized water, NaCl, KCl), eluent concentration (1–5 N), coagulant dose (1–6 g), Coagulant-eluate volume (20–120 mL), initial pH (6–10) and initial effluent concentration (3,100–7,693 mg/L). All the experiments were repeated at least thrice for consistency and the results averaged. The plot was made for the averaged value with the reproducibility greater than 98%.

2.4. Parameters evaluation

The coagulation ability of *C. tetragonolobus* was assessed in terms of residual color, and turbidity. All the parameters mentioned in Table 2 were measured using standard methods [26]. Color was measured using SL 218 double UV visible spectrophotometer (Elico—India) at λ_{max} 612 nm. Turbidity was measured using digital nephelo-turbidity meter 132 (Elico—India) and it was expressed in nephelometric turbidity units (NTU). pH is adjusted using digital pH meter MK.V.I (Elico—India).

3. *Cyamopsis tetragonolobus* (guar gum)

Guar gum is the uncharged natural gum. It contains 41% dry weight and acetone insoluble solids of the seeds. At least 75% of acetone insoluble solids of the endosperm are galactomannose and 12% being accounted for pentosan, protein, pectin, phytin, ash and dilute acid insoluble residues. The chemical analysis of the guar gum is shown in Table 3 [27]. The material contains 10%–13% moisture. The guargum lacks in uronic acid, which is generally found in other plant gums and mucilage [28]. The chemical structure of the guar gum is given in Fig. 1 [29].

Guar gum, which structurally comprises of a straight chain of D-mannose with a D-galactose side chain on approximately every alternate mannose unit, has a molecular weight of the order of 220,000. As a result of its wide range properties, guar gum is the most extensively used gum, both in food and industrial applications. It is an effective flocculant over a wide range of pH and ionic strengths. In the mining industry guar gum is used as a flocculant or flotation agent, foam stabilizer, Filtration and water treating agent. In the textile industry, it is used as a sizing agent and as a thickener for dyestuffs. The biggest consumer of guar gum is the paper industry where it Facilitates wet-end processing and improves the properties of the product [30].

Table 3
The chemical analysis of guar gum [27]

Components	Composition (Wt. %)
Nitrogen	0.67 corresponding with 3.5–4.0 proteins
Phosphorus	0.06
Ash	1.07
Water soluble polysaccharide	86.50
Water insoluble fraction	7.75
Alcohol sol. fraction (from 24 h Soxhlet extraction)	1.50

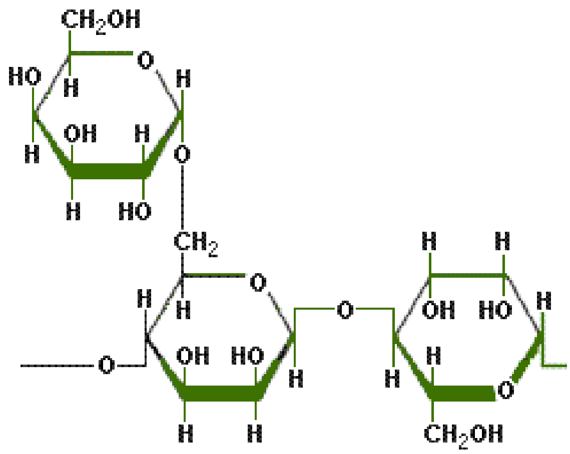


Fig. 1. Chemical structure of the guar gum [29].

4. Results and discussion

4.1. Characterization of Cyamopsis tetragonolobus (guar gum)

Comparing the FTIR spectra of the gum samples treated with 1 M KCl and 1 M NaCl, the peak intensity corresponding to adsorbed water at 1,640 cm^{-1} is greatly reduced in the 1 M KCl treated sample (Fig. 2). Moreover, the broad vibration around 3,340 cm^{-1}, which is attributed to intermolecular hydrogen bonding/O-H bond stretching, is reduced by a considerable amount compared to the control. The salt concentration showed a drastic effect on the intensity of the vibration at 3,340 cm^{-1}. This indicates that the intra molecular hydrogen bonds are greatly affected due to the presence of salts and this in turn can impact the characteristics of the gum. The intensities of the vibrations at 1,640 (adsorbed water), 1,152 (bending vibration mode of C- O in the pyranose ring), and 1,069 cm^{-1} (primary alcoholic CH_2 -OH stretching mode) are also affected by the increasing salt concentration [32].

4.2. Effect of eluent type and concentration

In 100 mL of, each of, various eluent namely deionized water, 1–5 N of NaCl and KCl, 5 g of *C. tetragonolobus* powder was suspended. The prepared coagulant –eluate was applied in a litre of PIE. It was observed that the color and turbidity removal efficiencies were 61% and 73%, respectively, in case of deionized water. When NaCl was utilized as an eluent, the removal was boosted with the concentration of the eluent till 4 N. The optimized type and concentration of eluent to treat a litre of PIE was concluded as 1 N KCl solution. From the Figs. 3(a) and (b) it was noticed that at 1 N KCl, the color and turbidity removal was 83.35% and 88.54%, respectively. The values were in declined nature when the concentration swelled up. The assumed reason may be that, the 1 N KCl might extract the maximum possible polysaccharaides from the known amount of *C. tetragonolobus*.

The broad vibration due the presence of intermolecular hydrogen bonding/O -H bond stretching is around 3,340 cm^{-1} in case of the water eluated sample > 1 M NaCl

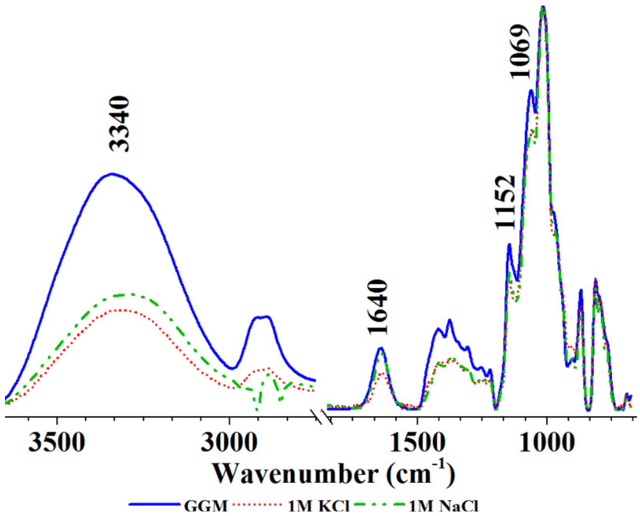
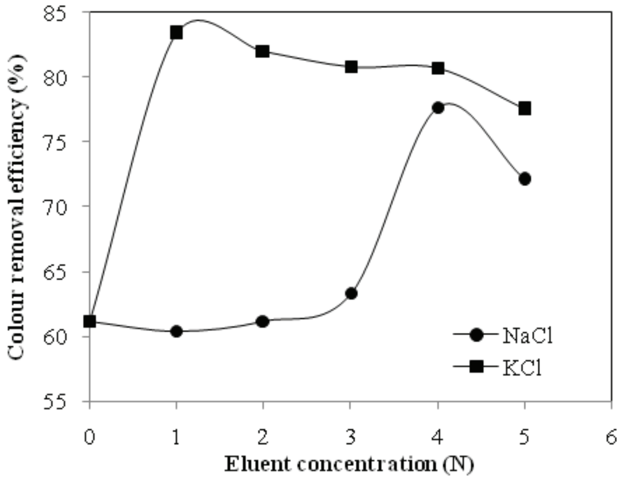


Fig. 2. FTIR spectra of pure guargum and guargum extracted using 1 MKCl and NaCl [31].



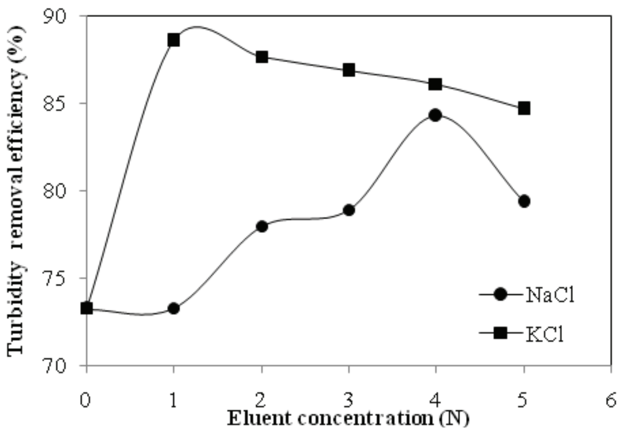


Fig. 3(a). Effect of eluent type and concentration on color removal efficiency. (b) Effect of eluent type and concentration on turbidityremoval efficiency.

Note: PIE volume: 1 L; Eluent: deionized water, 1–5 N NaCl, 1–5 N KCl; Coagulant dose: 5 g; Coagulant-eluate volume: 100 mL; Initial pH: 7.8 ± 0.2; Initial effluent concentration: 3,100 mg/L.

eluated sample > 1 M KCl eluated sample (Fig. 2). The influence of the eluent type and concentration on color and turbidity removal efficiencies were acknowledged through the intensity of peak in FT-IR. It was observed from result that the treatment efficiencies were increased with decrease in intensity value.

Further increasing ionic strength may denature the active compounds, which ended with lower removal efficiency. Identical results were highlighted in the treatment of water based paint industry wastewater using *S.potatorum* as a coagulant by varying the strength of the ionic solutions [19].

4.3. Effect of coagulant dose

The coagulant-eluate prepared with different doses of *C. tetragonolobus* (1–6 g) using 1 N of KCl was added in a PIE. The optimal coagulant dose to treat a litre of PIE was marked as 5 g. The removal efficiency at this juncture was 84.6% for color and 89.3% for turbidity. From the Fig. 4 it was clearly viewed that the color and turbidity removal was hiked with increase in the coagulant dose, till 5 g and beyond which it tapered. The reason behind this is that the increase in the coagulant dose resulted in larger amount active coagulant compounds which lead to the higher treatment efficiency. Similar results were marked in the treatment of paint industry wastewater using *C.opuntia* as a coagulant [20] and tannery industry wastewater using guargum [25].

4.4. Effect of coagulant –eluate volume

Different volume of coagulant-eluate (20–120 mL) prepared with 5 g of *C. tetragonolobus* was used in the treatment of PIE. The color and turbidity removal was in ascending trend with the increase in the volume of coagulant-eluate volume (Fig. 5). The logic behind this is that the larger volume contains more amounts of active components which removed the pollutants from PIE in larger

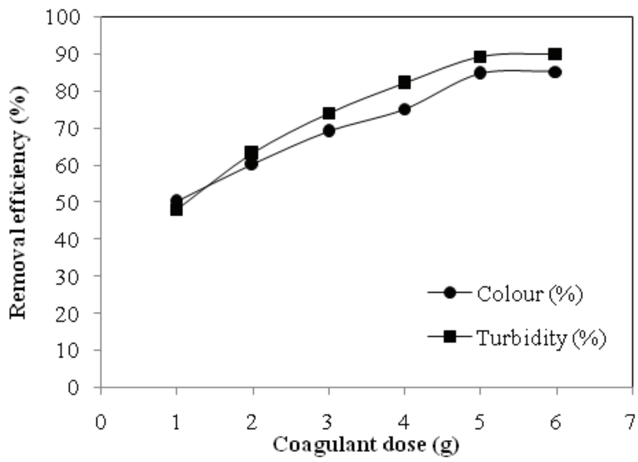


Fig. 4. Effect of coagulant dose on removal efficiency.

Note: PIE volume: 1 L; Eluent: 1 N KCl; Coagulant dose: 1–6 g; Coagulant-eluate volume: 100 mL; Initial pH: 7.8 ± 0.2; Initial effluent concentration: 3,100 mg/L.

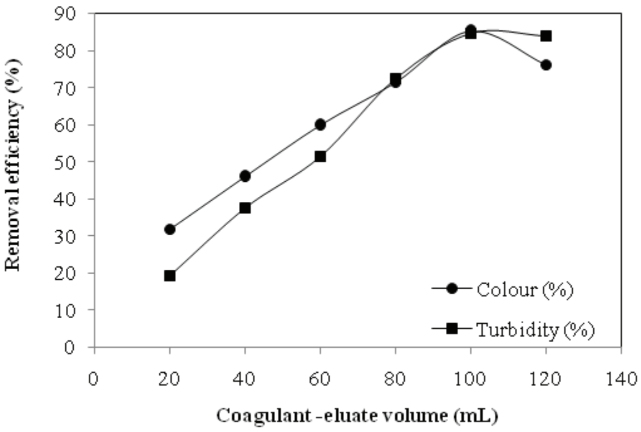


Fig. 5. Effect of coagulant-eluate volume on removal efficiency.
Note: PIE volume: 1 L; Eluent: 1 N KCl; Coagulant dose: 5 g; Coagulant-eluate volume: 20–120 mL; Initial pH: 7.8 ± 0.2; Initial effluent concentration: 3,100 mg/L.

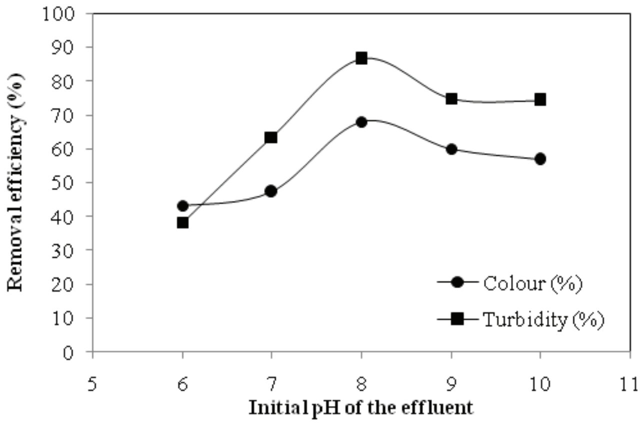


Fig. 6. Effect of initial pH of the effluent on removal efficiency.
Note: PIE volume: 1 L; Eluent: 1 N KCl; Coagulant dose: 5 g; Coagulant-eluate volume: 100 mL; Initial pH: 8; Initial effluent concentration: 3,100 mg/L.

quantity. Further increase in the eluate volume ended with plateau behavior. The coincidence in the results was identified in the removal of color, COD and turbidity from simulated paint industry wastewater by crab shells as a coagulant [21].

4.5. Effect of effluent initial pH

The actual pH of the prepared PIE was 7.8 ± 0.2. By adding the acid HNO_3/base NaOH the pH was varied to acidic and base region, respectively. The experiment could not be carried out below pH 5 because of the incidence of precipitation. Irrespective of the initial pH of the PIE, the treated effluent pH was in the range of 7 ± 0.4. The effect of initial pH (6–10) of the PIE on color and turbidity removal was studied (Fig. 6). The removal was in the increasing trend till pH 8, beyond that it declined. The maximum removal efficiencies (68% for color and 86.43% for turbidity) were observed at the optimum initial pH 8. The removal at acidic pH was in ascending trend due to the existence of -OH groups in the eluated coagulant. Adsorption and charge neutralization is the believed mechanism behind this. The results indicated that the treatment was preferred to conduct at the actual pH of the effluent itself.

The results were supported by the work done on the binding of Cd to *S. potatorum* seed proteins in aqueous solution [32]. The pre-treatment of winery wastewater and olive mill wastewater by coagulation, using a natural organic coagulant chitosan, showed the best performances achieved at the actual pH of the wastewater [33].

4.6. Effect of effluent initial concentration

Simulated PIE samples featuring five different initial concentration quantities of 3,100, 4,224, 5,650, 6,258 and 7,693 mg/L, were prepared and labeled as Sample numbers 1 to 5, respectively. The observed removal efficiency values showed marked improvement from Samples 1 to 5, demonstrating that pollutant removal accelerated as the initial concentration of effluent ascended from 3,100 to 7,693 mg/L.

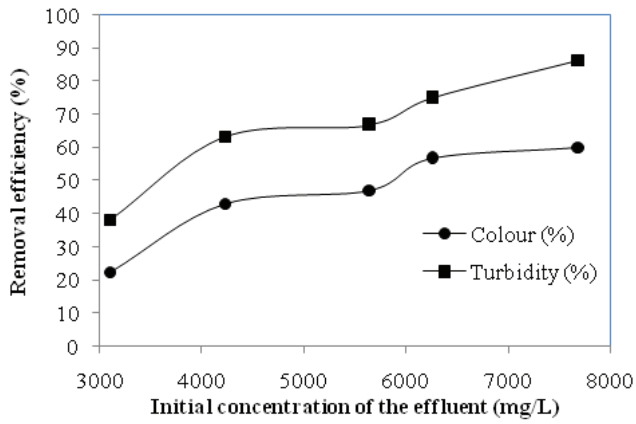


Fig. 7. Effect of initial concentration of the effluent on removal efficiency.
Note: PIE volume: 1 L; Eluent: 1 N KCl; Coagulant dose: 5 g; Coagulant-eluate volume: 100 mL; Initial pH: 8; Initial effluent concentration: 3,100–7,693 mg/L.

It is evident that a higher concentration of effluent, as in Sample no.5, was effective in promoting greater removal of pollutants: 60% and 86.43% for color and turbidity, respectively (Fig. 7). These results may be justified by hypothesizing that a higher concentration gradient acted as the driving force behind efficient utilization of the coagulant. The optimization of electrochemical treatment of PIWW [34] and decolorization of the brilliant green, using cactus fruit peel [35] also validated the above results.

The comparison of the performance of the treated PIE using other coagulants with guar gum was listed in Table 4. From the removal values it was confirmed that the guar gum could act as a better coagulant equivalent to chemical coagulant.

Table 4
Comparison of the characteristics of treated effluents under optimum conditions

Parameters	*S. potatorum*	*C. opuntia*	Alum	Ferric chloride	*C. tetragonolobus*
	% removal [19]	% removal [20]	% removal [19]	% removal [20]	% removal [present study]
Color	98.21	88.37	100	89.35	85.2
Turbidity	85.57	82.60	99.91	88.53	84.7

5. Conclusions

The results of the present study supported that the *C. tetragonolobus* (guar gum), perform well as a natural coagulant in the removal of pollutant from PIE. The optimized results proposed that to treat a litre of PIE, 100 mL of eluate extracted by using 5 g of guar gum with 1 N KCl at it actual pH (7.8 ± 0.2) exposed better removal efficiency. Being a biodegradable, eco friendly, abundance in nature, *C. tetragonolobus* (guar gum), could perform as a preferred substitute for the chemical coagulants.

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