

A Novel Method of Algal Based Water Treatment by Natural Coagulant “Alginates”

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Abstract: Waste water treatment is the major problem being faced in developing countries, like India presently, only about 10% of waste water generated is treated; the rest is discharged as it is into our water bodies the most commonly faced problem in disposal of waste water is their colour and turbidity. Among these, removal of colour is one of the major concerns in waste water treatment. For analysing synthetic textile waste water samples (Congo red), a standard jar test was conducted with the different initial concentration of 50, 100, 150, 200 and 250 mg/L with different initial pH of 4, and 6 in distilled water. These samples were treated with the different dose of calcium and different doses of alginate. Results of the study indicated that calcium alginate proved to be a very effective coagulant causing turbidity removals generally over 95%. In these samples concentration values as low as were achieved even at low doses of alginate. By increasing alginate doses and increasing residence time helps to improve the performance. Calcium alginates are used as a clarifier, foam stabilizer, emulsifiers.

Keywords: Turbidity, Clarifier, Calcium, Alginates, Coagulant

1. Introduction

Coagulation and flocculation are an initial process in water treatment for removal of suspended particles by destabilization. In general inorganic metals (such as alum, ferric chloride, lime, etc) and polymers (natural or synthetic polymer) are used as the coagulant aid. Alum (Aluminium sulphate) is the most common used coagulant for many years. The alum is dissolved in water, it destabilizes the particles is through hydrolysis, (so it is a hydrolysing metal salt coagulant) the aluminium ions, Al^{3+} that form, the colloidal particles are carried and neutralize the negative charges for stability. The aluminium ions hydrolyse and in the process form aluminium hydroxide, $Al(OH)_3$ precipitates when the water is slowly stirred the precipitates enmesh the destabilized particles to settle down. Polymers remove the particles by one or more reactive groups on the molecular chain adsorb onto the particles and destabilize them, this mechanism called bridging. The effectiveness of polymers does not necessarily increase with increased dosage [1]. The main disadvantages of coagulation by metal salts are the typical high quantities of chemicals needed, high quantity of sludge produced, and the significant change in pH during the treatment [1]. Another disadvantage of alum is the concern about the suspected role of aluminium in Alzheimer's disease [2]-[4].

Due to some negative impacts of the synthetic polymer on human health, the current research will focus on natural polymeric materials. The natural polymeric materials such as polysaccharides have been suggested because easily available, low cost, low molecular weight, and high shear stability. Additional advantages of this natural polyelectrolyte include safety for human health, biodegradability, and a

wider effective dose range of flocculation for various colloidal suspensions [5]. Hence, natural organic polymers have been suggested to replace inorganic coagulants in recent years [4].

The natural coagulants extracted from certain kind of plants such as Prosopis Juliflora, Cactus latifaria, Moringa oleifera, etc are used for water treatment. These coagulants are performed well in water of both high and low turbidity. In addition cactus extracts, chitosan and cationic starches were studied as alternative coagulants and results concluded that they have coagulation and flocculation capacity for turbidity removal [6]-[8]. From these studies, the natural coagulants are advantages than the inorganic metals and synthetic polymers.

In such a way alginate derived from marine brown algae. It is the natural polysaccharide. The polymer is formed by α -L glucuronic acid (G) and β -D mannuronic acid (M) monomers. In forming alginate the monomers make block structures of MM, MG, and GG. The relative abundance of these blocks in the alginate structure shows the reactions that alginates go through especially with metal cations, and hence the nature of the final product [9]. Alginate is the only polysaccharide, which naturally contains carboxyl groups in each constituent residue, and possesses various abilities for functional materials [10]. The alginate is reacting with polyvalent metal cations, especially calcium ions to produce strong gels or insoluble polymers [11]-[12].

The water treatment process is carried out in various types of equipment such as thickener, sedimentation, clarifier, etc are used for turbidity removal. Among these clarifiers is used for this research. Therefore the aim of the study was to determine the performance of a calcium alginate as a coagulant for

turbid water treatment using jar test apparatus and to find out its advantages and disadvantages in coagulation and flocculation process. The clarifier was designed from the performance of calcium alginate.

2. Materials and Methods

2.1 Algae Collection



(a) Sargassum sp 1



(b) Sargassum sp 2



(c) Turbinaria sp



(d) Kaapaphycous allverzii (red algae)

Figure 1: Various species (a,b,c,d) of brown algae and red algae

Different species of brown algae (*Sargassum* sp, *Turbinaria* sp) and Red Algae (*kappaphycous allverzii*) were collected in coastal waters of a Mandapam, Tamil Nadu (Bay of Bengal) in January 2013 shown in Figure 1 (a,b,c,d). The collection of samples was done by cutting the thallus with a knife near the rhizoid. Algae were washed with seawater and dried by the sun at ambient temperature and stored in bags with ventilated site.

2.2 Alginate Preparation



Drying (hot air oven)



After extraction



Filtration

Figure 2: During sodium alginate preparation

The sample was washed abundantly with water and dried for 30 h at 65°C. Alginates were extracted according to the procedure of [Taratra Andree Fenoradosoa *et al.*, 2010]. Twenty-five grams of dried algae were soaked in 800 mL of 2% formaldehyde during 24 h at room temperature, washed with water and then added to 0.2 M HCl (800 mL) and left for 24 h. After this time, the samples were washed again with distilled water. Then Alginates were extracted with 2% sodium carbonate during 3 h at 100°C. So, the soluble fraction was collected by filtration and polysaccharides were precipitated by three volumes of ethanol 95%. Sodium alginate collected was washed twice with 100 mL of acetone, dried at 65°C and dissolved in 100 mL of distilled water. It was then precipitated again with ethanol (v/3v) and dried at 65°C. (The Figure 2 shows about *Drying, After extraction Filtration*).

2.3 Sample Preparation

The synthetic textile waste water sample was prepared by adding a known amount of Congo Red (shown in Figure 3) with the various initial concentration of 50, 100, 150, 200 and 250 mg/L with different pH of 4, 5 and 6 in distilled water and mixing for 1 h. The Congo red sample surface had a negative charge with -9.28 mV of zeta potential. Each 500 mL sample was treated using different doses of calcium and alginates for this experiment.



Figure 3: Synthetic textile waste water

2.4 UV-spectrophotometer Analysis

Initially, the UV-spectrophotometer is standardized by measuring the absorbance of distilled water at known standard wavelength (510 nm) of the dye sample. Standard dye solutions (10, 20, 30 mg/L, etc.) were prepared and their absorbance is noted using UV-spectrophotometer. For Congo red, the maximum wavelength was set to 510 nm. Then the absorbance of the sample of unknown concentration was noted. The graph is plotted between absorbance and concentration which gives a straight line. From the graph, the equation was found to determined concentration of the unknown (after treatment) sample.

2.5 Experimental Procedure

The calcium in coagulation process it had the ability to compress the double layer and to reduce repulsive forces between colloid/colloid, polymer/colloid, and polymer/polymer pairs [9]. Here both the Congo red and the alginate were negatively charged. Calcium added first and alginate added next throughout this test. A standard jar test apparatus was used for this experiment shown in Figure 4 (a).



Figure 4: (a) Conducting jar test



Figure 4: (b) Floc formation

Calcium as calcium chloride and alginate as sodium alginate was used for this experiment. The calcium dosed varied between 1 to 6 mg/L, next alginate dosed varied between 1 to

6 mg/L. Mixing condition for each sample employed during the experiments with following order: 5 min rapid mixing at 100 rpm for calcium dosing, 5 min rapid mixing at 100 rpm for alginate dosing, then 20 min slow mixing at 40 rpm and finally for settling 30 min. The supernatant after sedimentation was filtered using Whatman no. 42 filter paper shown in Figure 4 (b). The filtrate was analyzed for absorbance using UV-spectrophotometer at a maximum wavelength 510 nm, the initial concentration of 50, 100, 150, 200 and 250 mg/L which provides better performance in treatment.

3. Results and Discussion

3.1 Alginate Yield

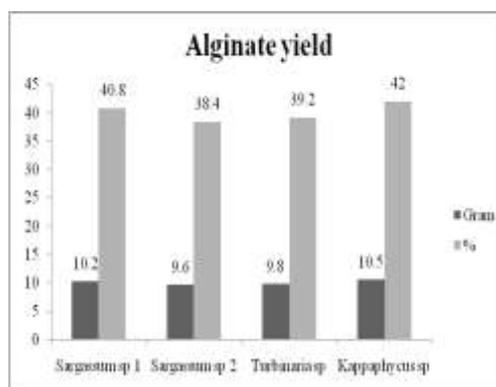


Figure 5: Alginate Yield from Various Species of Brown and Red Algae

To determine alginate yield of dry seaweed, about 25g of dry seaweeds was analysed. After extraction process sodium alginate content was obtained to be 10.2, 9.6, 9.8 and 10.5 g in Sargassum sp 1, Sargassum sp 2, Turbinaria sp and kappaphycous allverzii respectively. The extraction of sodium alginate from seaweed was about 40.8, 38.4, 39.2 and 42% of Sargassum sp 1, Sargassum sp 2, Turbinaria sp and kappaphycous allverzii respectively, which shows the potential application of seaweed for the production of natural coagulant (represented in Figure 5).

Generally worldwide accepted drinking water turbidity limit is less 1 NTU and for human consumptive purpose turbidity limit is less than 5 NTU. In this study, a final turbidity of less than 1 NTU was selected. When the calcium and alginate were added, the large flocs were formed, it was observed visually. The flocs settled rather quickly because it is strong and heavy.

3.2 Calibration Curve for Congo red Dye

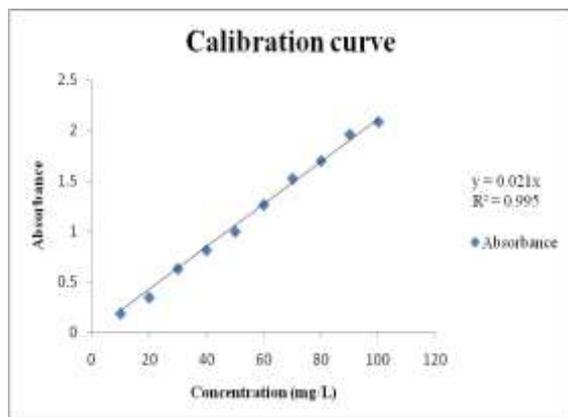


Figure 6: Concentration vs. Absorbance for Congo red dye

The graph (Figure 6) shows the equation to find the final concentration of synthetic textile waste water (after treatment). The equation is $y = 0.021x$

Where, y : Absorbance, x : Concentration

$$\text{Concentration (x)} = y / 0.021$$

Above equation was used to find the final concentration.

3.3 Effects of calcium and alginates

3.3.1 Initial concentration of 250-200mg/L

The performance of initial concentration of synthetic textile waste water of 250 and 200 mg/L as shown in Figure 7 (A,B,C,D,E,F) the concentration region of 0 to 250 mg/L to be shown in Figure 8 (A,B,C). The figure clearly shows when calcium and alginate were added, the concentration values were fell near 10 and 9.8 mg/L in 250 and 200 mg/L of synthetic textile waste water respectively. From the graph as the dose of alginate increased with fixed calcium dosage the efficiencies of dye removal also increased. On the other hand the applied calcium in relation to the dye removal. The effectiveness of calcium dose depends on alginate dose was studied. The greatest dye removal efficiencies were achieved at 6 mg/L of calcium dosage and 6 mg/L alginate dosage in 250mg/L of the synthetic textile waste water and 6 mg/L of calcium dosage and 5 mg/L alginate dosage in 200mg/L of the synthetic textile waste water. Calcium alginate forms improper gel formation at low calcium dosage.

The synthetic textile waste water sample was negatively charged the low calcium concentration was not enough to neutralize sample so the dyes remain stable. 6 mg/L of calcium dosage requires 6 and 5 mg/L of alginate dosage in 250 and 200 mg/L of synthetic textile waste water respectively was enough to achieve required concentration levels. For 6 mg/L of calcium dosage with 6 and 5 mg/L of alginate dosage, the percentage of dye removal values were calculated and removal rates were as over 95%. This result shows in high initial concentration the calcium alginate act as the very effective coagulant in a different combination of calcium and alginate doses.

3.3.2 Initial concentration of 150-100mg/L

The results for the initial concentration of synthetic textile waste water of 150 and 100 mg/L for different calcium and alginate doses were shown in below Figure 8 (G,H,I,J,K,L). From graph low final concentration near 4.6 and 7.6 mg/L

were achieved at 150 and 100 mg/L of synthetic textile waste water for 6 mg/L of calcium dosage at different alginate doses studied. The alginate doses level at 150 and 100 mg/L were smaller than alginate dosage level at 250 and 200 mg/L. The optimum alginate dosage range at 250 and 200 mg/L was 6 and 5 mg/L for 6 mg/L of calcium dosage respectively. On the other hand, this optimum alginate range at 150 and 100 mg/L was 4 and 3 mg/L for 5 mg/L of calcium dosage respectively. The percentage dye removal values in 150 and 100 mg/L were calculated and over 94% or 95 % for 5 mg/L of calcium dosage. For low calcium dosage, the percentage dye removal values were calculated, below 90% was achieved in both 150 and 100 mg/. In low calcium dosage, dye removal was lower but still varied depends on different alginates dosage were studied. This result shows in medium initial concentration the calcium alginate act as a very effective coagulant in a different combination of calcium and alginate doses.

3.3.3 Initial concentration of 50mg/L

The final concentration value for the initial concentration of 50 mg/L synthetic textile waste water at different calcium and alginate doses were shown in Figure 9. The performance of lower concentration increased when compared to the samples of higher concentration. The optimum concentration of alginate was 2 mg/L for various mg/L of calcium dosage for synthetic textile waste water samples. The final concentration values achieved as near 2.5 mg/L, with various calcium dosage. The efficiency of dye removal ranged from 94 to 96% depending on the calcium and alginate dose.

The dye removal efficiency was increased due to an absence of enough particles to constitute nuclei for the flocs to form. Then the calcium alginate gel formation is the main mechanism because when the stage of gel formation or after gel formation, it combines and capture the particles to form heavy particles, it is enough to settle down. However, the flocs were not heavy particles it is not enough to settle down and separate. Even calcium alginate gels might have also contributed to some extra turbidity.

With these observations low concentration samples may not enough to make floc formation, so by using the higher viscosity of alginates gave the better result than a lower viscosity of alginates in final concentration values. In higher viscosity of alginate molecular weight is high it increases dye removal efficiency. Molecular weight increase is directly related to the polymer chain length. So when it increases, the polymer's bridging ability increases

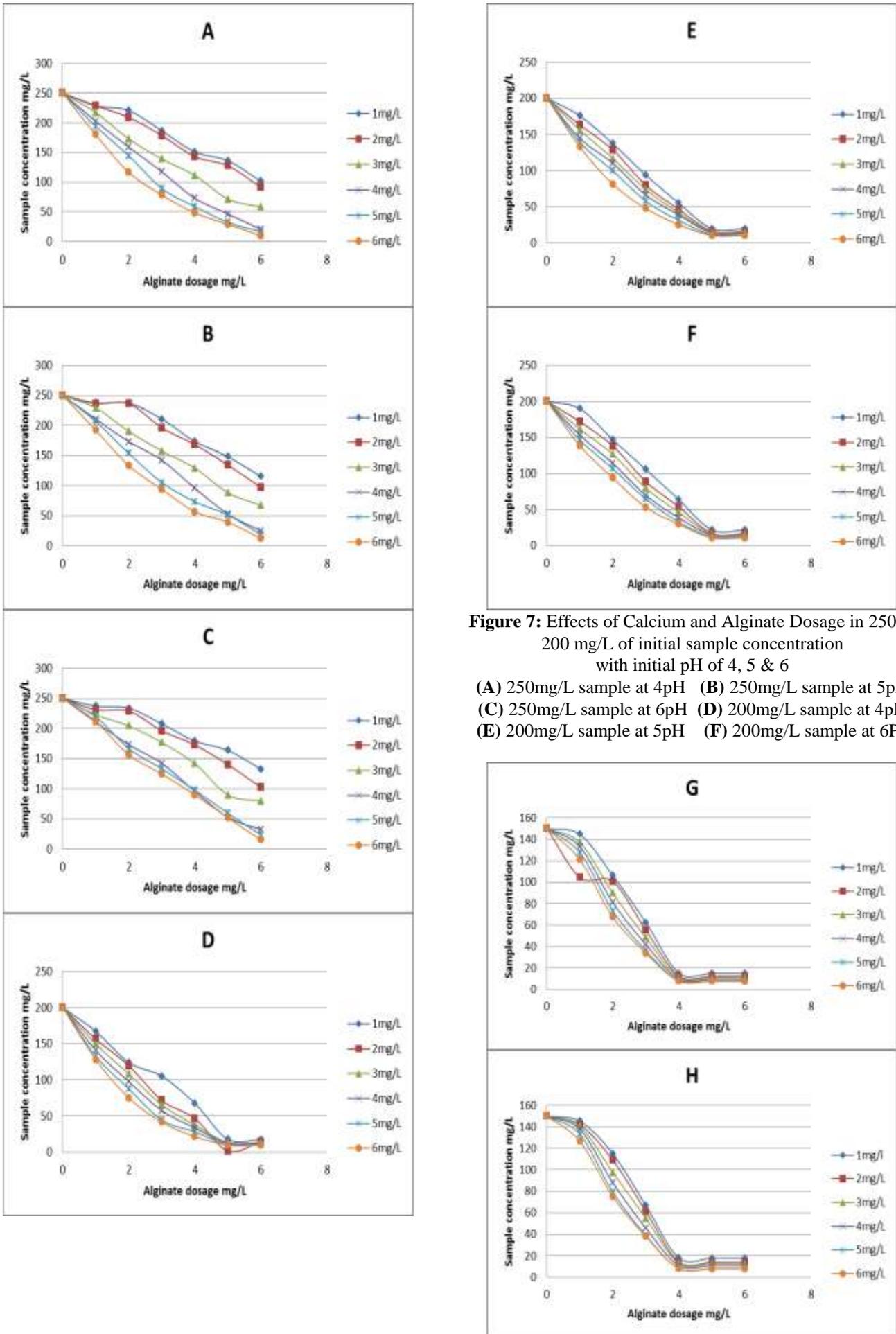


Figure 7: Effects of Calcium and Alginate Dosage in 250 & 200 mg/L of initial sample concentration with initial pH of 4, 5 & 6
 (A) 250mg/L sample at 4pH (B) 250mg/L sample at 5pH
 (C) 250mg/L sample at 6pH (D) 200mg/L sample at 4pH
 (E) 200mg/L sample at 5pH (F) 200mg/L sample at 6pH

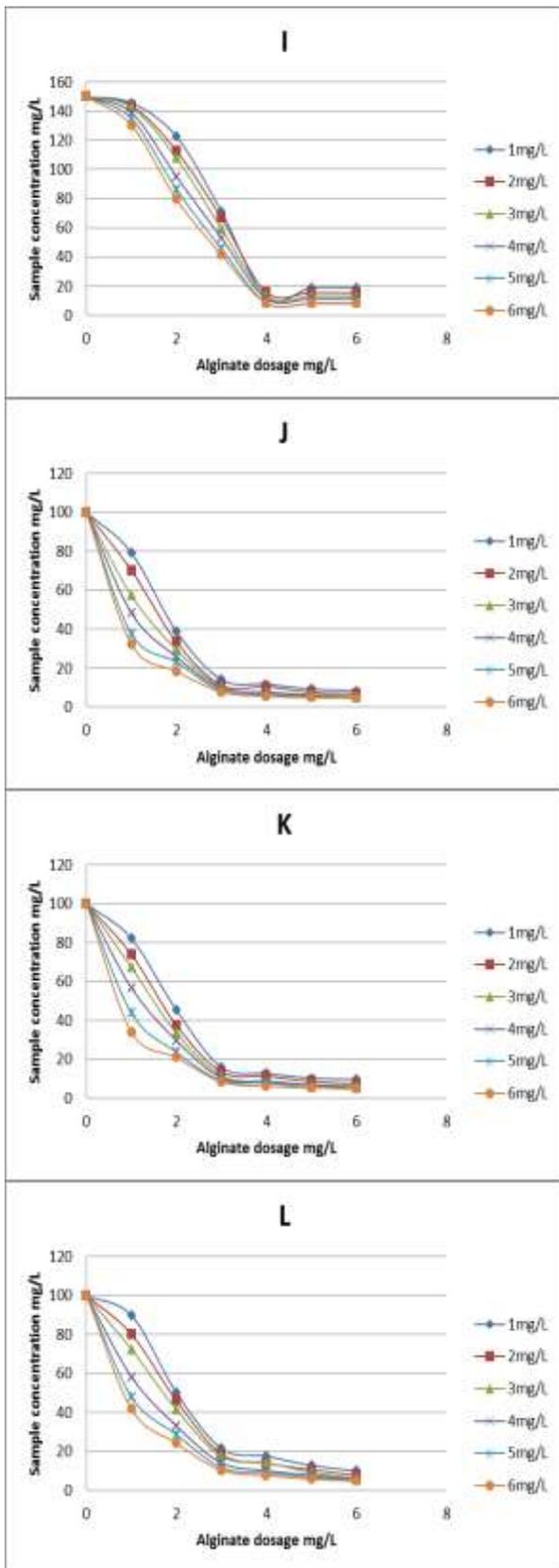


Figure 8: Effects of Calcium and Alginic Acid Dosage in 150 & 100 mg/L of initial sample concentration with initial pH of 4, 5 & 6

(G) 250mg/L sample at 4pH (H) 150mg/L sample at 5pH
 (I) 150mg/L sample at 6pH (J) 100mg/L sample at 4pH
 (K) 100mg/L sample at 5pH (L) 100mg/L sample at 6pH

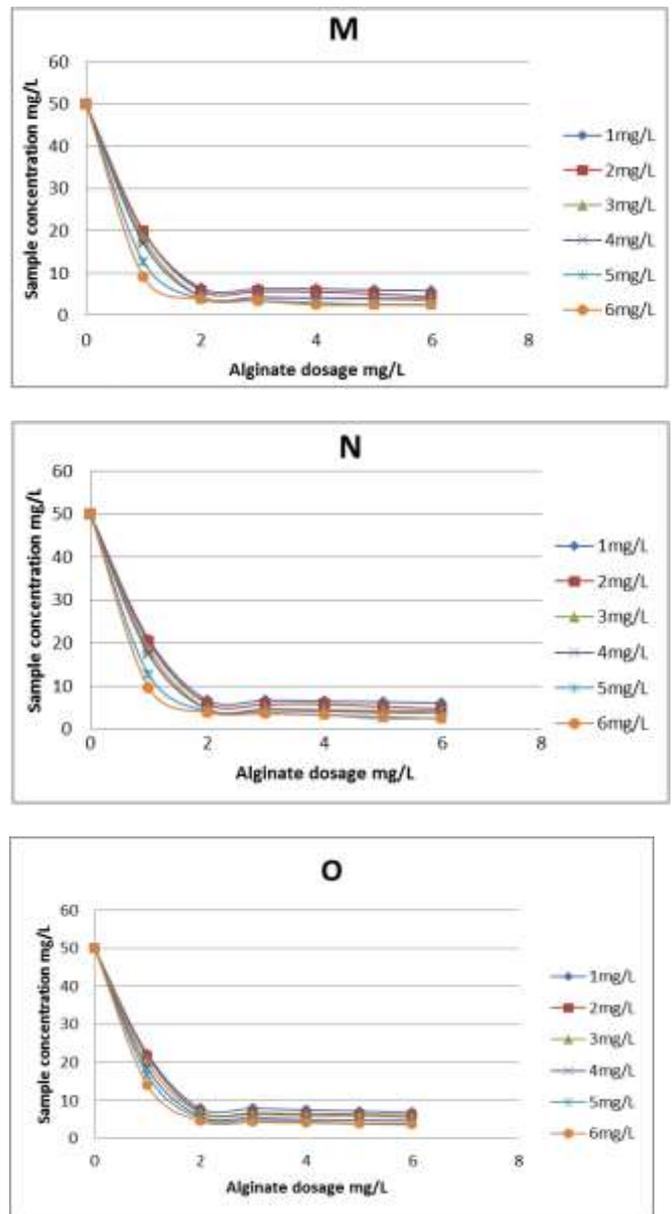


Figure 9: Effects of Calcium and Alginic Acid Dosage in 50 mg/L of initial sample concentration with initial pH of 4, 5 & 6

(M) 50mg/L sample at 4pH (N) 50mg/L sample at 5pH
 (O) 50mg/L sample at 6pH

3.4 Summary of best performance conditions for dye removal

So far the results clearly showed that calcium alginate can act as a coagulant for the removal of dye from the synthetic textile waste water sample. Neither calcium nor alginate could achieve the targeted concentration levels, therefore their action together was deemed necessary. The negative surface charge particles and used polysaccharide, which is alginic acid necessitate a positively charged agent that is calcium added to the system. The monomeric units, guluronic acids, and mannuronic acids have pKa values of 3.65 and 3.38, respectively [13]. Therefore, calcium ion is required for the alginic acid to approach and bind to the surface. So in dye removal system by the calcium alginate, surface charge neutralization by calcium is the first step. So better performance of the system was calcium is added prior to

alginate. The action of alginate is the formation of calcium alginate gel, or bridging the gap between the particles by one of the two mechanisms is believed, which is more effective at high calcium doses [14].

Table 1: Dye removal % at different initial concentration with different initial pH

Initial Concentration mg/L	pH	Alginate Dosage mg/L	Calcium Dosage mg/L	Final Concentration mg/L
250	4	2	4	3.9
	5	2	5	4.1
	6	2	6	4.5
200	4	3	5	8.3
	5	3	4	9.2
	6	3	6	10.3
150	4	4	5	8.1
	5	4	5	8.1
	6	4	5	8.5
100	4	5	6	9.9
	5	5	5	11.4
	6	5	6	10.8
50	4	6	6	10
	5	6	6	12
	6	6	6	15

The target was set as low concentration value could be achieved by the calcium alginate dose combinations in most cases. Table.1 presents the achieved lowest concentration values and the associated calcium and alginate concentration. Low target value could be reached, at various calcium and alginate doses for 250, 200, 150, 100 and 50 mg/L initial concentration samples. All these studies show that calcium alginates as the better coagulant in the system.

4. Conclusion

The study showed the performance of alginate was highly dependent on the calcium concentration and initial concentration of the sample. At 250 & 200 mg/L of initial concentration, the coagulant performed well and achieved the value of 3.9 and 8.3 mg/L of final concentration respectively. The calcium and alginate were performed at 150, 100 & 50mg/L of initial concentration were good. Using higher viscosity alginate and prolonged rapid mixing for low concentration samples may reduce economic feasibility. Finally, that calcium alginate acted as a potential coagulant and it eliminates the traditional coagulant.

References

[1] D.J. Nozaic, S.D. Freese, P. Thompson, Longterm experience in the use of polymeric coagulants at Umgeni Water, *Water Sci. Tech. Water Supply* 1 (2001) 43–50.
 [2] M. Ozacar, I.A. Sengil, Evaluation of tannin biopolymer as a coagulant aid for coagulation of colloidal particles, *Colloid Surf. A* 229 (2003) 85–96.
 [3] C. Huang, S. Chen, J.R. Pan, Optimal condition for modification of chitosan: a biopolymer for coagulation of colloidal particles, *Water Res.* 34 (2000) 1057–1062.
 [4] H. Salehizadeh, S.A. Shojaosadati, Extracellular biopolymeric flocculants: recent trends and

biotechnological importance, *Biotechnol. Adv.* 19 (2001) 371–385.
 [5] S. Kawamura, Effectiveness of natural polyelectrolytes in water treatment, *J.AWWA* 83 (1991) 88–91.
 [6] J. Zhang, F. Zhang, Y. Luo, H. Yang, A preliminary study on cactus as coagulant in water treatment, *Process. Biochem.* 41 (2006) 730–733.
 [7] R. Divakaran, V.N.S. Pillai, Flocculation of kaolinite suspensions in water by chitosan, *Water Res.* 35 (2001) 3904–3908.
 [8] S. Pal, D. Mal, R.P. Singh, Cationic starch: an effective flocculating agent, *Carbohydr. Polym.* 59 (2005) 417–423.
 [9] H. Aylin Devrimci, A. Mete Yuksel, F. Dilek Sanin, Algal alginate: A potential coagulant for drinking water treatment. *Desalination.* 299 (2012) 16-21.
 [10] A. Ikeda, A. Takemura, H. Ono, Preparation of low-molecular weight alginic acid by acid hydrolysis, *Carbohydr. Polym.* 42 (2000) 421–425.
 [11] G.T. Grant, E.R. Morris, D.A. Rees, P.J.C. Smith, D. Thom, Biological interactions between polysaccharides and divalent cations: the egg-box model, *FEBS Lett.* 32 (1973) 195–198.
 [12] A.H. King, Brown seaweed extracts (alginates), in: M. Glicksman (Ed.), *Food Hydrocolloids*, vol. II, CRC Pres, Boca Raton, FL, 1983, pp. 115–188.
 [13] T.A. Davis, B. Volesky, A. Muccib, A review of the biochemistry of heavy metal biosorption by brown algae, *Water Res.* 37 (2003) 4311–4330.
 [14] N.E. Simpson, C.L. Stabler, C.P. Simpson, A. Sambanis, I. Constantinidis, The role of the CaCl₂ – glucuronic acid interaction on alginate encapsulated βTC3 cells, *Biomaterials* 25 (2004) 2603–2610.