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EFFICACY OF ALGINATE EXTRACTED FROM MARINE BROWN ALGAE (*SARGASSUM SP.)* AS A COAGULANT FOR REMOVAL OF DIRECT BLUE2 DYE FROM AQUEOUS SOLUTION

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ABSTRACT

The coagulation potential of alginate extracted from marine brown algae, *Sargassum sp.* for the removal of Direct Blue 2 dye from aqueous solution was studied. Extracted alginate was characterised by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) techniques. Batch coagulation tests were carried out by using standard Jar test apparatus to study the influence of initial pH (4 – 10), coagulant (alginate) dosage (10 – 60 mg l^{-1}), initial concentration of dye (100 – 500 mg l^{-1}) and calcium dosage (1 – 6 g l^{-1}) on removal of dye. The maximum dye removal was observed as 86.1 % at initial dye concentration of 200 mg l^{-1}, 6 g $l^{-1}$of calcium dose, 40 mg $l^{-1}$of alginate dose and pH 4. The Sludge Volume Index (SVI) was examined at the maximum dye removal condition and compared with Alum. The kinetic study reveals that the coagulation process for the removal of Direct Blue 2 dye follows second order kinetic model. The obtained results were compared with the literature available on the application of various seaweeds for wastewater treatment methods and their efficiency. Based on the investigation, it is evident that the alginate extracted from *Sargassum sp.* can be used as an effective novel coagulant for the removal of Direct Blue 2 dye from aqueous solution.

Keywords: *Sargassum sp*, Brown algae, Direct Blue 2 dye, Coagulation

1. Introduction

India has 8085 kilometres long coastal line, in which plenty of seaweed species are available. About 700 species of marine algae have been identified in the various parts of coastal line of India and nearly 60 species are commercially important (Sajid *et al.*, 2003). The seaweeds are categorized into three types, namely the Chlorophyta (green algae), the Phaeophyta (brown algae) and the Rhodophyta (red algae). The seaweed resources are exclusively utilized for the production of commercially and industrially important phycocolloids

such as carrageenan, agar, alginates, soda ash, Alginic acid, iodine (Kaladharan *et al.*, 1999). These phytochemicals are widely used as gelling, stabilizing, thickening agents in food, confectionary, pharmaceutical, dairy, textile, paper, paint and varnish industries. These wide variety of seaweeds were found to have a remarkable biochemical compounds that enables antibacterial, antiviral, antifungal, cytotoxic, and larvicidal potentials (Aseer *et al.*, 2009). Certain protein rich sea weeds are used in palatable condition in the form of soup, salad, curry etc. Jelly, jam, chocolate, pickle and wafer can also be prepared from certain seaweeds. Marine algae are also used in different parts of the world as animal feed and fertilizer for crops as they contain more than 60 trace elements, carbohydrate, iodine, bromine, vitamin and some bioactive substances (Kaliaperumal *et al.*, 1997). Apart from these uses, seaweeds have the potential for use in wastewater treatment process. Among various process oriented industries, textile industry is one of the major sources of coloured wastewater. A dye is used to impart colour to a material, of which it becomes an integral part of textile industry which affects the quality of water. Azo dyes are typically used in textile processing and paper manufacturing industries. A massive amount of azo dyes from these sources is discharged into natural waterways (Su *et al.*, 2011). The wastewater generated from different stages of textile processing contains large quantity of pollutants can cause harmful effects to the environment if released without proper treatment. These pollutants gave several direct and indirect harmful effects like immune suppression, respiratory, circulatory, central nervous and neurobehavioral disorders presage as allergy, autoimmune diseases, multiple myeloma, leukemia, vomiting, hyperventilation, insomnia, profuse diarrhea, salivation, cyanosis, jaundice, quadriplegia, tissue necrosis, eye (or skin) infections, irritation to even lung edema (Verma *et al.*, 2012). Ultimately the removal of dye from the textile wastewater becomes an important task and the dye removal techniques can be classified into two categories, namely Destructive and Non-Destructive (Fernandez *et al.*, 2010) as presented in Table 1**.**

Table 1. Classification of dye removal techniques

Destructive methods	Non-destructive methods
Biodegradation	Adsorption
Advanced oxidation processes (AOP) - Fenton process, Ozonation, Sonolysis, Electrochemical oxidation, Electrical discharges, Wet air oxidation Photolysis, Photo catalysis	Sedimentation
	Filtration
	Coagulation
	Electrocoagulation

Among all the treatment methods, Coagulation process is the simple and economical one. The detailed comparison of advantages and disadvantages of various physical and chemical process of wastewater treatment was discussed by Chuah *et al.*, (2003). In coagulation process, selection of suitable coagulant is important, which includes considerations like availability, cost, quantity and suitability.

The coagulants like ferric chloride and aluminum sulfate (alum) for wastewater treatment were used in full-scale for several decades (Jiang J-Q, 2015). However, these conventional coagulants can cause the major problem of producing large quantity of hazardous sludge which contains metal ions that lead to harmful effects to human, animals and plants. The recent studies on coagulant reveals that the metal salts like Alum has several drawbacks, such as Alzheimer's disease associated with residual aluminum in treated water and production of large sludge volumes. It has also been reported that the reaction of aluminum with natural alkalinity present in the water leads to a reduction of pH and low efficiency of coagulation in cold waters. To overcome these problems involved in chemical coagulants, in the recent years the studies on natural coagulants produced or extracted from plants gain momentum (Patel *et al.*, 2013). Hence, it becomes essential to search for a novel natural coagulant, which can be used in small quantity and produce less amount of nonhazardous sludge. In the present study, an attempt has been made to identify the coagulation potential of alginate extracted from the marine brown algae, *Sargassum sp.* for the effective removal of Direct Blue 2 dye from aqueous solution.

2. Material and methods

2.1. Preparation of synthetic dye solution

Direct Blue 2 is an azo dye having a molecular formula $C_{32}H_{21}N_6Na_3O_{11}S_3$ and a molecular weight of 830.71 g mol^{-1}. The dye stock solution was prepared by dissolving 1 g of Direct Blue 2 dye in 1 l of double distilled water. Later, it was diluted by using distilled water as per to the concentration required and pH was adjusted by adding 0.1 M NaOH solution and 0.1 M HCl. The synthetic wastewater samples were prepared with various initial dye concentrations of 100, 200, 300, 400 and 500 mg l^{-1} with different pH of 4, 5, 6, 8, 9 and 10. The concentration of Direct Blue 2 dye was determined by using a UV-spectrophotometer (Systronics - 119, India) at a wavelength corresponding to maximum absorbance of 611 nm.

2.2. Marine algae collection

Marine Brown algae (*Sargassum sp.*) were collected from coastal waters (Bay of Bengal) of Mandapam (9.27^o N 79.12^o E), Tamil Nadu, India. Collection of samples was done by cutting the thallus with a knife near the rhizoid. The collected samples were washed with seawater in the site. The washed samples are stored in bags with ventilation before transporting it to the laboratory for further processing.

2.3. Alginate extraction

The sample was washed abundantly with water and dried for 30 h at 65 °C. Alginates were extracted by following the procedure reported by Fenoradosoa (Fenoradosoa *et al.*, 2010). The alginate industry extraction protocol is divided into five steps: acidification, alkaline extraction, solid/liquid separation, precipitation and drying (Vauchel *et al.*, 2008). Twenty-five grams of dried algae were soaked in 800 ml of 2 % formaldehyde for 24 h at room temperature, washed with water and then added to 0.2 M HCl (800 ml) and left for 24 h. After which, the samples were washed again with distilled water. Alginate was extracted with 2 % sodium carbonate at 100 °C for 3 h. The soluble fraction was collected by filtration and polysaccharides were precipitated by three volume 95 % of ethanol. The precipitated Sodium alginate was washed twice by 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 monomers present in the alginate extracted from the marine brown algae are D-mannuronic acid and L-guluronic acid (Kharkwal *et al.*, 2012). The carboxyl groups present in the alginate can be able to react with any functional group and forms gel structure (Ikeda *et al.*, 2000). The important characteristics of alginate are the ability to react with polyvalent metal cations and to form strong insoluble polymer gel. When alginate was interacted with calcium ion, it forms an “egg-box” structure. The coagulation process can be enhanced by any one of the following mechanism: charge neutralization along with the bridging of particles or by the gel formation of calcium and alginate. Calcium alginate gel combines with the dispersed particle irrespective of the charge and leads to flocculation (Simpson *et al.*, 2004). Fenoradosoa *et al.,* 2010 reported that the weight-average molecular weight and number-average molecular weight of the sodium alginate extracted from marine brown algae as 5.528 x 10^5 g mol^{-1} and 3.852 x 10^5 g mol^{-1} respectively. The pKa values of D-mannuronic acid and L-guluronic acid was reported as 3.38 and 3.65 respectively (Davis *et al.*, 2003). The Zeta-potential (surface charge) of alginate was reported as -60 mV for 500M and -50 mV for 500G (Minami *et al.*, 2010). The Charge density, θ of alginate gel with calcium chloride (for M/G=1) was reported as -9.00 x 10^{-3} $mol.dm^{-3}$ (Inukai *et al.*, 1999).

2.4. Characterization of alginate

Fourier Transform Infrared (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM) techniques were used to characterize the alginate extracted from the brown algae *Sargassum sp.* The FT-IR spectroscopy (Thermo Nicolet, AVATAR 330) was employed to determine the functional groups present in the alginate. FT-

IR spectra was taken both for raw and dye loaded samples. The infrared spectrum of alginate was recorded as KBr discs in the range of 4000 – 400 cm^{-1}. Scanning Electron Microscopy (TESCAN, VEGA 3) was used to characterize the surface structure and morphology of the raw and dye loaded samples of alginate.

2.5. Experimental procedure

A standard jar test apparatus (Dolphin CIC-304, SCIENCIL India) was employed to carry out the experiments. Calcium as calcium chloride and alginate as sodium alginate were used. The calcium dosed varied between 1 to 6 g l^{-1} and alginate dosed varied between 10 to 60 mg l^{-1}. 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. The filtrate was analyzed for absorbance using UV-spectrophotometer (Systronics-119, India) at a maximum wavelength 611 nm. The percentage dye removal was calculated by using equation (1).

$$\text{Dye removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i and C_f are the initial and final dye concentration, respectively.

The Sludge Volume Index (SVI) is the volume occupied by 1 gm of suspension after 30 mins settling. The SVI in ml g^{-1} was determined by following the standard method (Part 2710 D) prescribed by American Public Health Association (APHA, 1998) using the equation (2). At the maximum colour removal condition, the settled sludge volume after 30 min settling was determined (Part 2710 C) and the suspended solids concentration of a well-mixed sample of the suspension was measured (Part 2540 D). The same procedure was repeated for the commercial coagulant (Alum).

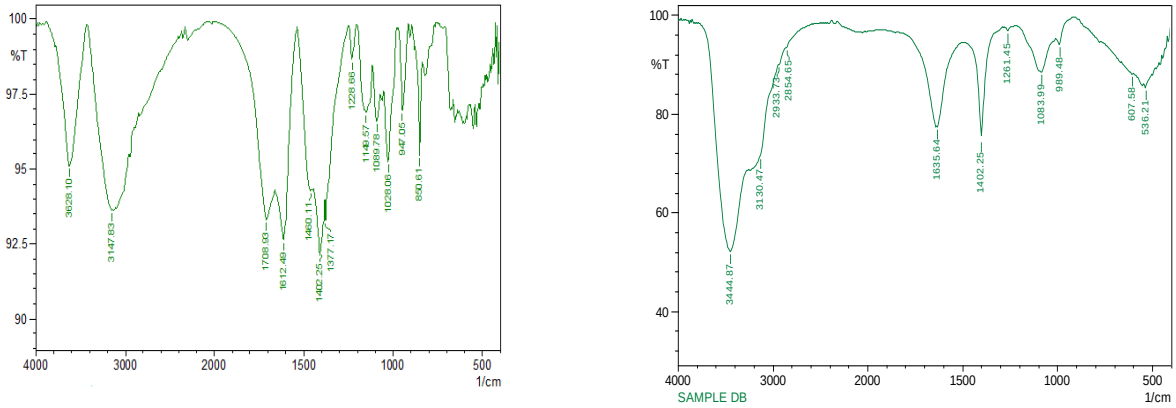
$$\text{SVI} = \frac{\text{Settled sludge volume, ml } l^{-1} \times 1000 \text{ mg } g^{-1}}{\text{Suspended solids, mg } l^{-1}} \quad (2)$$

The calcium in coagulation process has ability to compress the double layer and to reduce repulsive forces between colloid/colloid, polymer/colloid and polymer/polymer pairs (Devrimci *et al.*, 2010). In this study, the Direct Blue 2 dye is positive charge and the alginate is negatively charged. Calcium added first and alginate added next throughout this test. The initially added Calcium chloride forms free Ca^{2+} ions and binding the cross linkages of functional groups in the alginate polymer chain (Patel *et al.*, 2012 and Rezende *et al.*, 2007). In the mechanism of coagulation, the very long polymer chain molecules on the surface of particles may form loops and the end of these loops may attach with another particle, which forms a bridge between the two particles. This is the bridging mechanism of flocculation and the charges of particle and alginate do not play any important role in this mechanism (Singh *et al.*, 2003).

3. Results and discussion

3.1. FT-IR spectrum analysis

The FT-IR spectrum of raw alginate from *Sargassum* sp is presented in Fig. 1 (a). A broad band at 3468 cm^{-1} and 3628 cm^{-1} was assigned to hydrogen bonded OH. A sharp and strong absorption bond at 1612 cm^{-1} representing the C=C stretch. The band at 1460 cm^{-1} represents the methylene C-H stretch. A major band in the region 1708 $cm^{-1}$and 1697 cm^{-1} indicate the presence of a C=O group (carbonyl group) and this confirms the nature of alginate (Fenoradosoa *et al.*, 2010). Fig. 1 (b) represents the FTIR spectrum of sludge containing alginate and Direct Blue 2 dye. A broad band 3444 cm^{-1} represents the amino phenyl group which is due to the presence of Direct Blue 2 dye in the sludge (John Coates., 2000).

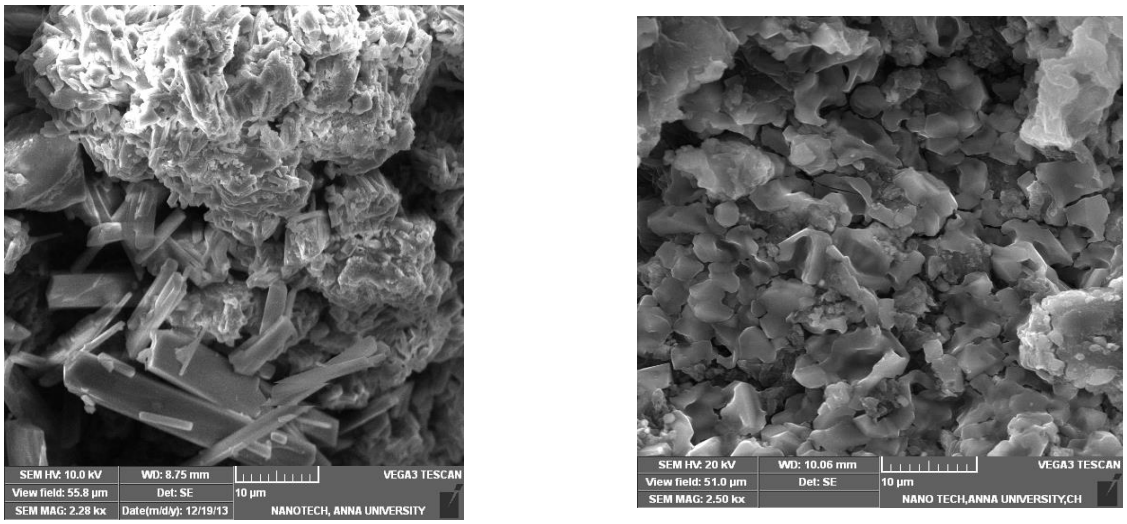


(a) (b)

Figure 1. FTIR spectra of (a) raw and (b) dye loaded alginate

3.2. SEM analysis

The morphology of the raw and dye loaded alginate surface was characterized by SEM analysis. Fig. 2(a) depicts the outer layer of raw alginate which possesses fine perforations and spines on it. It can be noted from Fig. 2(b) that after coagulation, the surface of the alginate was clogged by the dye molecules.



(a) (b)

Figure 2. SEM image of alginate (a) raw and (b) after coagulation

3.3. Effect of pH

The pH of the system is influencing the coagulation uptake of Direct Blue 2 dye molecule due to its influence on the surface charge properties of the calcium alginate, and ionization/dissociation of the dye molecule. The maximum percentage removal of Direct Blue 2 dye was found to be 86.1 % at pH 4. The effect of pH on percentage dye removal is presented Fig. 3(a).

3.4. Effect of calcium and alginate dose

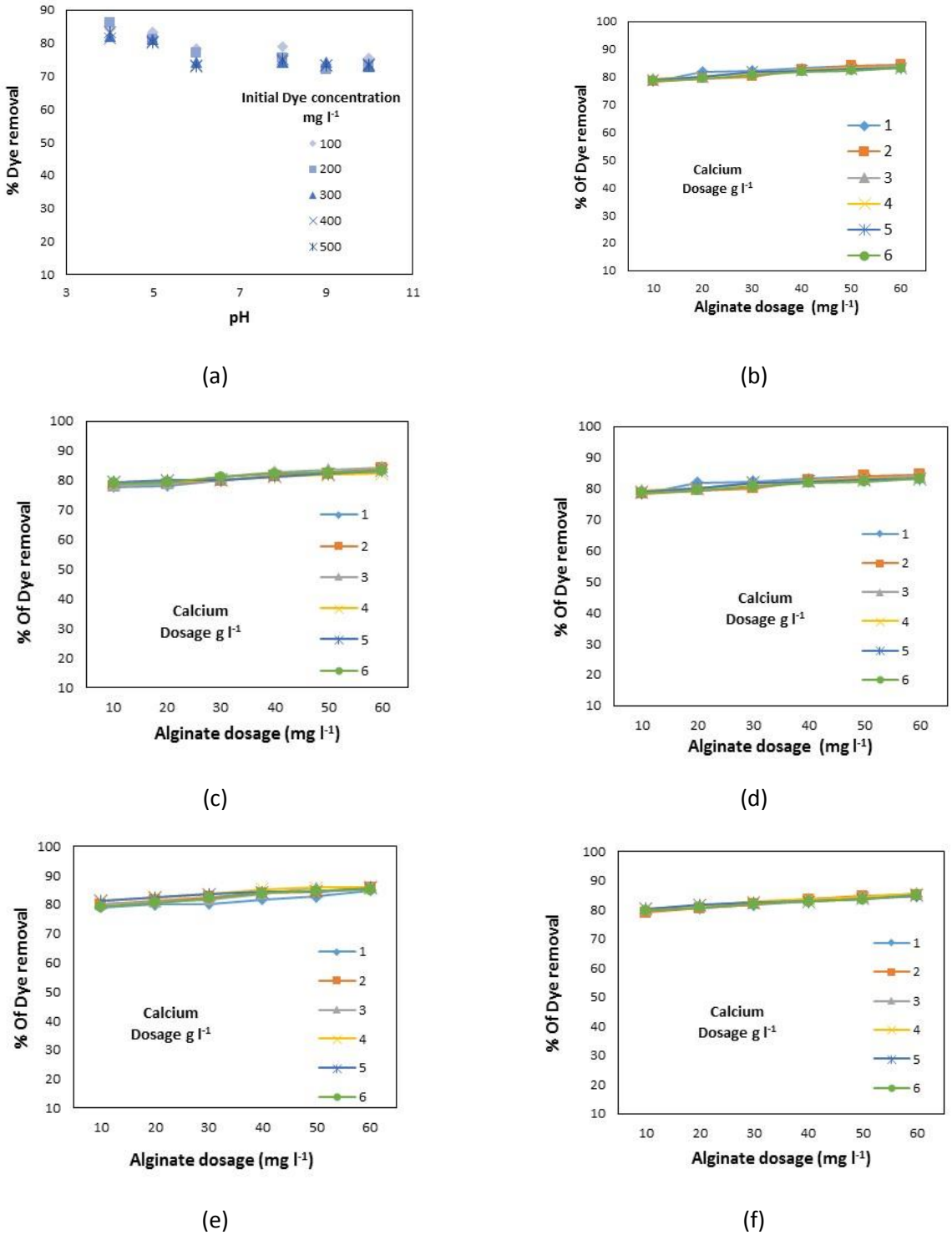


Figure 3. Effect of (a) pH and Effect of calcium and alginate dose on initial dye concentration at pH 4 (b) 100 mg l^{-1}, (c) 200 mg l^{-1}, (d) 300 mg l^{-1}, (e) 400 mg l^{-1}, (f) 500 mg l^{-1}

The effect of calcium and alginate dose on dye removal was studied by varying the initial dye concentration (100 to 500 mg l^{-1}) at pH 4 and the results are presented in Fig. 3(b) to 3(e). It can be noted from the figures that the increase in alginate dose increases the percentage dye removal for all calcium dose levels studied. Further, it can be noted that the dye removal is significant at low initial dye concentrations (i.e., 100 mg l^{-1}) although the calcium and alginate dose are less. However, when the initial dye concentration increases the low calcium dose is not effective in dye removal. The maximum dye removal (86.1 %) for initial dye concentration studied (i.e., 200 mg l^{-1}) was achieved at 6 g $l^{-1}$of calcium dose, 40 mg l^{-1} alginate dose and pH 4. During the experimentation, it was observed that the calcium alginate gel formation was not appropriate at low calcium doses. The optimum conditions for Direct Blue 2 dye removal at various initial dye concentrations at pH 4 is presented in Table 2.

Table 2. Optimum condition for Direct Blue 2 dye removal at pH 4

Initial dye conc. C_i (mg l^{-1})	Alginate dose (mg l^{-1})	Calcium dose (mg l^{-1})	% Dye removal
100	30	6	84.3
200	**40**	**6**	**86.1**
300	30	6	82.1
400	30	6	81.3
500	30	6	83.4

3.5. Sludge volume index

Sludge Volume index (SVI) is commonly used to observe the settling characteristics of activated sludge and other biological suspension (Chethana *et al.*, 2015). However, in the present study, the SVI is used to compare the performance of Alginate as a coagulant with the commercially available coagulant (Alum) in the aqueous dye solution. The SVI was obtained as 2.14 ml g^{-1} for the maximum dye removal (86.1 %) for initial dye concentration of 200 mg l^{-1}, 6 g l^{-1} of calcium dose, 40 mg l^{-1} alginate dose and pH 4. Similarly, for the same dye removal percentage (86%) the Alum dose was found to be 14.2 g l^{-1} and the SVI was obtained as 16.43 ml g^{-1}. Hence, it is evident from the experimental results that the quantity of sludge produced by Alum was more compared to Alginate and the alginate dose is much lower than the conventional chemical coagulant. However, it should be noted that the SVI values obtained are quite low compared to the values reported in literature which is due to the fact that in the present study, the SVI was studied in aqueous dye solution.

3.6. Coagulation kinetics

Coagulation kinetics for the removal of Direct Blue 2 dye using alginate as a coagulant was studied. It was observed that during coagulation process the rate of removal of dye is proportional to the initial dye concentration and the amount of calcium alginate complex. A first order and second order rate equation was examined with the experimental data (Nnaji *et al.*, 2014). The solution for first order equation is given in equation (3)

$$\log\left(\frac{C_i}{C_0}\right) = -kt \qquad (3)$$

Where Ci is initial dye concentration, C_0 is Concentration of dye after time's' minutes and k is first order rate constant (min^{-1}).

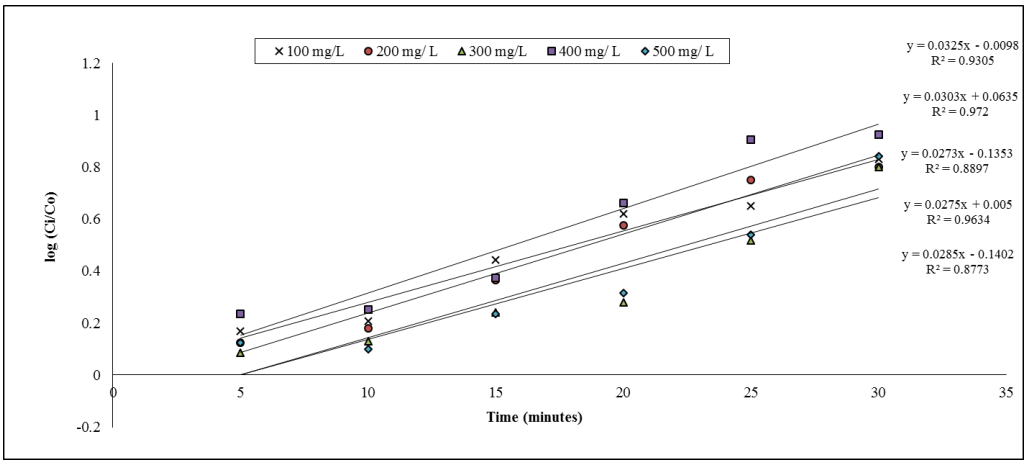
The solution for Second order equation is given in equation (4)

$$\frac{1}{C_o} - \frac{1}{C_i} = k't \quad (4)$$

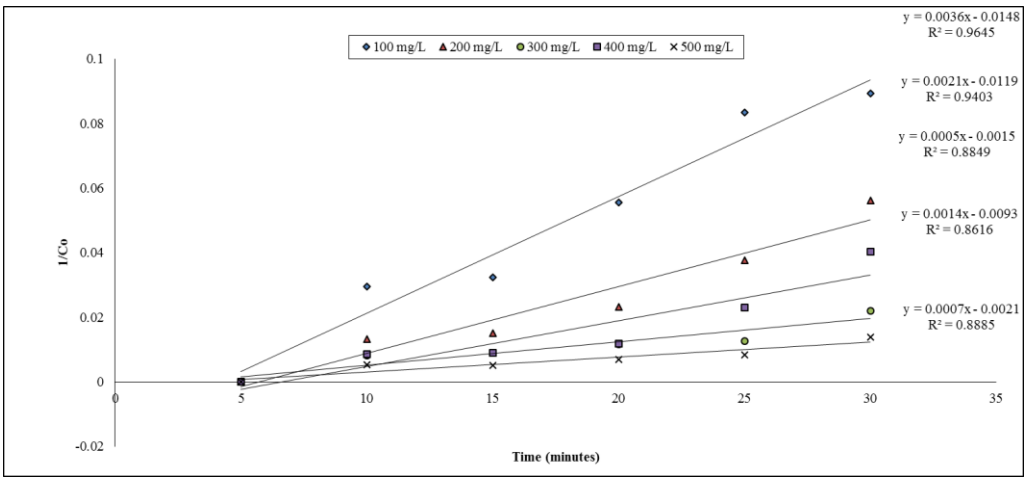
Where k' is second order rate constant (l mg^{-1} min^{-1})

The plot for first and second order kinetics to the experimental data with various initial dye concentrations was shown in Fig. 4 (a) and 4 (b). From the figure, the first order equation showed higher value of intercept which clearly reveals that the coagulation process did not obey first order kinetics. Hence the coagulation process for colour removal of Direct Blue 2 dye solution using algal alginate followed a second order kinetics.

On comparing with other processes, coagulation is the very simple process where the process parameters are easily controllable. Table 3 presents the wide application of seaweed in waste water treatment at various condition and the potential usage of various seaweed extract and their effectiveness were compared with the present study. It can be noted that the alginate extracted from *Sargassum* seaweed has the ability to act as coagulant for the effective removal of Direct Blue 2 dye.



(a)



(b)

Figure 4. Coagulation kinetics plot (a) First order (b) Second order

Table 3. Potential usage of seaweeds in waste water treatment process

Seaweed	Treatment process	Pollutant removed	Efficiency	References
Protonated or Ca-form Sargassum seaweed biomass	Bio sorption	Trivalent and Hexavalent Chromium	70%	David *et al.*, 1998
Sargassum binderi (Brown seaweed)	Batch sorption	Basic yellow 11	99%	Pie *et al.*, 2009
Enteromorpha	Adsorption	Malachite green	94.74%	Jayaraj *et al.*, 2011
*Amphiroa foliacea (*Red seaweed*)*	Biosorption	Reactive blue 4,	94%	Siew-Ling *et al.*, 2011
*Caulerpalentillifera (*Green seaweed*)*	Batch sorption	acid yellow 25	70%	Wong *et al.*, 2011
		basic yellow 11	98%	
Ascophyllum nodosum	Anaerobic batch digestion	Copper	76%	Muhammad *et al.*, 2013
Mixed algae	Adsorption	Hexavalent Chromium	85 %	Gandhi *et al.*, 2013
Isochrysis galbana Chlorella.Sp	Biosorption	Textile wastewater	55%	Mithra *et al.*, 2012
Sodium Alginate from Sargassum seaweed	***Coagulation***	***Synthetic wastewater containing Direct blue dye***	***86.1 %***	***Present study***

4. Conclusion

The coagulation potential of alginate extracted from *Sargassum sp.* for the removal of Direct Blue 2 dye from aqueous solution was studied. The experiments were carried out in a standard jar test apparatus in order to evaluate the influence of various parameters such as pH, initial dye concentration, calcium dose and alginate dose on dye removal. Maximum dye removal (86.1 %) was achieved with the optimum conditions as: pH 4, alginate dose of 40 mg l^{-1}, calcium dose of 6 g l^{-1} for the initial dye concentration of 200 mg l^{-1}. The Sludge Volume Index (SVI) at maximum dye removal condition using alginate as a coagulant was found to be 2.14 ml g^{-1}, whereas for the same dye removal condition, 14.2 g l^{-1} of Commercial coagulant (Alum) was required and the SVI of Alum was found to be 16.43 ml g^{-1} .The kinetic study on coagulation process showed that the process suitably fits well in second order kinetics reaction equation. It is evident from the results obtained that the alginate extracted from *Sargassum sp.* has the potential for the removal of Direct Blue 2 dye from aqueous solution.

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