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Effective removal of Reactive Magenta dye in textile effluent by coagulation using algal alginate

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ABSTRACT

Textile dyeing industrial wastewater needs simplified and efficient treatment method for dye removal. Coagulation is a technique among several treatment techniques available for the removal of color in the textile effluent. In coagulation process, inorganic metal salts such as alum, ferric chloride, and synthetic polymers are generally used as a coagulant. Because of the drawbacks involved in metal salts, more research is motivated on natural biopolymeric materials. In this study, an efficient novel biopolymeric coagulant alginate, which is extracted from the *Sargassum* sp., a marine brown alga from the coastal region of Gulf of Mannar, is used for the removal of Reactive Magenta dye in the real-time textile industrial wastewater. The Reactive Magenta dye present in the wastewater is treated using the conventional jar test with alginate as a coagulant. The raw alginate and dye loaded alginate was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy techniques. The effect of alginate dose, calcium dose, and settling time was investigated. It was observed that the maximum color removal of 92.7% at optimum conditions of 30 mg/L of alginate dose, 4 g/L of calcium dose, and in a neutral pH was achieved. Based on this study, it has been validated that the alginate, a natural biopolymeric compound extracted from brown algae *Sargassum* sp., can be used an effective coagulant for Reactive Magenta dye removal from the real-time textile wastewater.

Keywords: Reactive Magenta dye; Textile effluent; Coagulation; *Sargassum* sp.

1. Introduction

In the developing countries of the world, wastewater discharged from industries is customarily liquidated into a contiguous living area or water bodies. A distinctive industrial discharge may contain a lot of substances which may be injurious to the environment. The World Health Organization has specified safe bounds for the discharge of effluents into the environment. In order to fulfill the standards specified by the regulating bodies, the industries are forced to treat the effluents in an efficient way before disposal [1]. Commonly, the textile wastewater is reasonably a complex mixture and is highly adaptable, involving many pollutants. This wastewater is a mixture of dyes, surfactants, fixing agents, oxidizing agents, recalcitrant chlorinated compounds, salts, heavy metals, dispersing agents, and smoothing agents. Wastewaters are extremely colored because of the presence of dyes that have not been fixed to the fiber during the dyeing process [2]. They are also characterized by high levels of chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, salinity, temperature, turbidity, toxic chemical compounds, total dissolved solids, and total suspended solids [3,4]. Furthermore, many textile dyes or by-products are themselves toxic,

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carcinogenic, mutagenic, and/or teratogenic. Table 1 lists the characteristics of textile wastewater from different stages of textile industry processes. It is observed that the finishing process involved in dyeing and printing section releases large quantity of colored effluent, which need an intensive treatment before discharge. The coagulation process is a well-established method for the efficient physical treatment of synthetic and industrial effluents that contains color, turbidity, suspended solids, dissolved solids, etc. Coagulation process is a primary and commonly used unit process in wastewater treatment. The principle involved in this process is the destabilization of stable colloidal particles in suspension, such that they can agglomerate into settleable flocs. Because of the simplicity and promising results with wide applications in treatment of surface and wastewater treatment facilities, coagulation is the frequently used technique in water treatment [5]. Metal salts such as aluminum and iron salts are the more commonly used coagulants together with synthetic organic polymers. Normally, coagulants are often expensive and the intensification of process leads to abrupt change in pH of the water, which can lead to its secondary contamination. Additionally, the sludge formed during coagulation process is non-biodegradable which contains metal salts and complex inorganic mixtures. Conventionally, residual aluminum ions present in the treated water is the source of Alzheimer's disease. To overcome these complications, natural coagulants, mainly polysaccharides available naturally as parts of plants and secretions of animals, are found to be more useful products and considered eco-friendly in contrast with inorganic coagulants [6]. Commonly used natural coagulants are mainly extracted from *Moringa oleifera, Phaseolus vulgaris*, and *Strychnos potatorum* [7].

In recent times, usage of some natural polymers such as alginate for the treatment of various types of wastewater has been reported. In particular, *Sargassum* sp., a brown alga, have rich source of alginate and shown promising results with respect to wastewater treatment. Alginate is derived from marine brown algae. It is a natural polysaccharide. Alginate is the only polysaccharide, which naturally contains carboxyl groups [9]. The polymer is formed by α-L-guluronic acid (G) and β-D-mannuronic acid (M) monomers. These polymers have found great industrial use due to their ability to form a gel with divalent cations such as Ca^{2+} and Sr^{2+} (except Mg^{2+}) [10]. The ability of alginate to react with polyvalent metal cations, especially calcium ions to produce strong gels or insoluble polymers made to choose this as a coagulant for wastewater treatment [11]. A comparison of natural coagulants over conventional chemical coagulants is presented in Table 2.

The literature review revealed that the researchers studied algal alginate as coagulant for wastewater treatment [13,14]. However, removal of dye from real-time textile effluent using alginate as coagulant which is extracted from the brown algae *Sargassum* sp. has not yet been studied. Reactive Magenta dye is commonly used in the dyeing

Table 1
Characteristics of wastewater during textile manufacturing [8]

Textile processes	Expected characteristics of wastewater
Fiber manufacturing	It mainly contains large amount of organic compounds, which contribute to BOD and COD It also contains suspended solids, which are mainly loose fibers
Spinning and weaving	It usually contains sizing agents such as starch, polyvinyl alcohol, wax, acrylic size, loose fiber, etc. All these components contribute to high amount of BOD, COD, and SS
Pretreatment—desizing, scouring, bleaching and mercerizing	It mainly constitutes more alkalinity and detergent from scouring process, sizing chemicals
Dyeing and printing	It possesses mainly dyes, pigments, dyeing auxiliaries and chemicals used during dyeing It contains BOD, COD, SS, heavy metals, and most importantly the color which is easily visible even at low concentrations

Table 2
Advantages of natural coagulants over conventional chemical coagulants [12]

Parameters	Natural coagulants	Conventional chemical coagulants
Cost	Sustainable and economical	Complex and expensive
Toxicity	Non-toxic to environment	Highly toxic
Corrosiveness	Non-corrosive to the materials	Highly corrosive due to alkalinity
Sludge characteristics	Small amount of non-hazardous and biodegradable sludge	Large amount of hazardous and non-biodegradable sludge
pH	Do not alter the pH of water under treatment	More changes in pH due to metallic salts
Sensitiveness	Provides rapid flocculation and decantation	Provides slow flocculation and decantation
Fragrance	Acts as a deodorant agent forming insoluble complexes with organic species such as proteins and carbohydrates	Offensive odor due to decomposed chemicals in the sludge

of cotton fabric. In this study, the alginate was extracted from the brown algae *Sargassum* sp. and the coagulation potential of alginate was tested with the real-time textile industrial colored wastewater containing the Reactive Magenta dye.

2. Materials and methods

2.1. Alginate extraction and wastewater sample

The brown algae *Sargassum* sp. were collected from the coastal waters (Bay of Bengal) in Mandapam, Tamil Nadu. The samples were collected by cutting the thallus with a knife near the rhizoid. The collected samples were washed with seawater in the site and stored in bags with ventilation before transporting it to the laboratory for further processing. The algae samples received in the laboratory were washed abundantly with tap water and dried in sunlight for 3 h. Later, the samples were dried for 30 h at 65°C in hot air oven. The alginate extraction procedure is divided into the following five steps [15]:

- Acidification,
- Alkaline extraction,
- Solid/liquid separation,
- Precipitation, and
- Drying

The procedure reported by Fenoradosoa et. al [16] was followed to extract the alginate from the algae. 25 g of dried algae were soaked in 800 mL of 2% formaldehyde for 24 h at room temperature and washed with water. Later, 800 mL of 0.2 M HCl was added to the sample and left for 24 h. The samples were washed again with distilled water, and the alginates were extracted with 2% sodium carbonate at 100°C. The soluble fraction was collected by filtration, and polysaccharides were precipitated by three volumes of ethanol 95%. Alginate collected 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 textile effluent from the dye bath containing Reactive Magenta dye was collected from a local industry. The concentration of dye was determined using a UV-spectrophotometer (Systronics-119, India) at a wavelength corresponding to maximum absorbance of the respective dye. The effluent was characterized in terms of dye concentration and pH, and the results are presented in Table 3.

Reactive Magenta dye is the anionic dye which has the absorption maxima of 520 nm. Reactive Magenta dye is mainly used in cotton textile dyeing industry [17,18].

Table 3
Characteristics of textile wastewater

Parameter	Reactive Magenta
Concentration of dye (approximately)	100 color units
pH	4.6
Absorbance, nm	520
Temperature, °C	30

2.2. Characterization of alginate

The alginate extracted from the brown algae *Sargassum* sp. was characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The FTIR spectroscopy (Thermo Nicolet, AVATAR 330) was employed to determine the functional groups present in the alginate. FTIR was done both for raw and dye-loaded samples. The infrared spectrum of alginate was recorded as KBr discs in the range of 4,000–400 cm^{-1}. SEM (TESCAN-VEGA3, Czech Republic) was used to characterize the surface structure and morphology of the raw and dye-loaded samples of alginate.

2.3. Jar test experiment

Batch scale studies were carried out using alginate extracted from *Sargassum* sp. for removal of dye from aqueous solution. Conventional jar test apparatus (Dolphin CIC-304, Sciencil India) was employed, and all the experiments were performed in triplicates in 1,000 mL beakers containing 500 mL of dye solution by following the standard procedure. Calcium as calcium chloride and alginate as extracted algal sodium alginate were used for the experiment. The calcium dose varied between 1 and 6 g/L, whereas the alginate dose varied between 10 and 60 mg/L. Calcium was added first and then alginate was added for all the experiments. The initially added calcium chloride produces Ca^{2+} ions which act as a binding material between the cross linkages of functional groups in the alginate polymer chain [19,20]. The experiment for each sample was carried out in the following order: 5 min rapid mixing at 100 rpm for calcium dosing, 5 min rapid mixing at 100 rpm for alginate dosing, followed by 20 min slow mixing at 40 rpm, and 30 min for settling. The supernatant after sedimentation was filtered using Whatman no. 42 filter paper. The filtrate was analyzed using UV-spectrophotometer [21]. The experiments were carried out for initial dye concentration of 1,000 mg/L. Percentage color removal was calculated by Eq. (1).

$$\text{Color removal \%} = \frac{C_i - C_f}{C_i} \tag{1}$$

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

For Reactive Magenta, a definite wavelength of 520 nm, the maximum absorbance of the real-time effluent, was obtained. Color intensity of the original effluent was arbitrarily taken to be 100 units, calibration curve was plotted then by diluting the original effluents, and the pH was maintained as 7 by adding 0.1 N NaOH, color intensity being taken to be equal to the percentage of original effluents in dilute sample. The final concentration of dye was estimated with the help of these absorbance data.

3. Results and discussion

3.1. SEM analysis

The morphology of the alginate surface was characterized by SEM analysis, and the images are presented in Fig. 1(a).

It can be observed from Fig. 1 that the outer layer of alginate possess fine perforations and spines on it [13]. Fig. 1(b) obtained after coagulation process depicts the smooth surface due to gel formation and binding of dye particles on the surface of porous alginate in the coagulation process.

3.2. FTIR analysis

The FTIR spectrum of the raw alginate from *Sargassum* sp. and dye-loaded alginate are presented in Figs. 2(a) and (b). In Fig. 2(a) (raw alginate), a broad band between 3,468 and 3,628 cm^{-1} was attributed to hydrogen bonded OH. A sharp and strong peak at 1,612 cm^{-1} represents the C=C stretch. The peak at 1,460 cm^{-1} indicates the methylene C–H stretch. A major peak in the region 1,708 and 1,697 cm^{-1} indicates the presence of a C=O group (carbonyl group) and this confirms the nature of alginate [13,16]. In Fig. 2(b), the wave number 1,598 cm^{-1} corresponding to the C=C stretching of the benzene ring and a stretch between 1,700 and 1,600 cm^{-1} represent the C=O group in alginate. A stretch at 3,329 cm^{-1} shows the presence of double azo chain –C=N– which confirms the presence of Reactive Magenta dye [22].

3.3. Effect of calcium and alginate dose

The effect of calcium and alginate dose on color removal of a real-time textile effluent containing Reactive Magenta

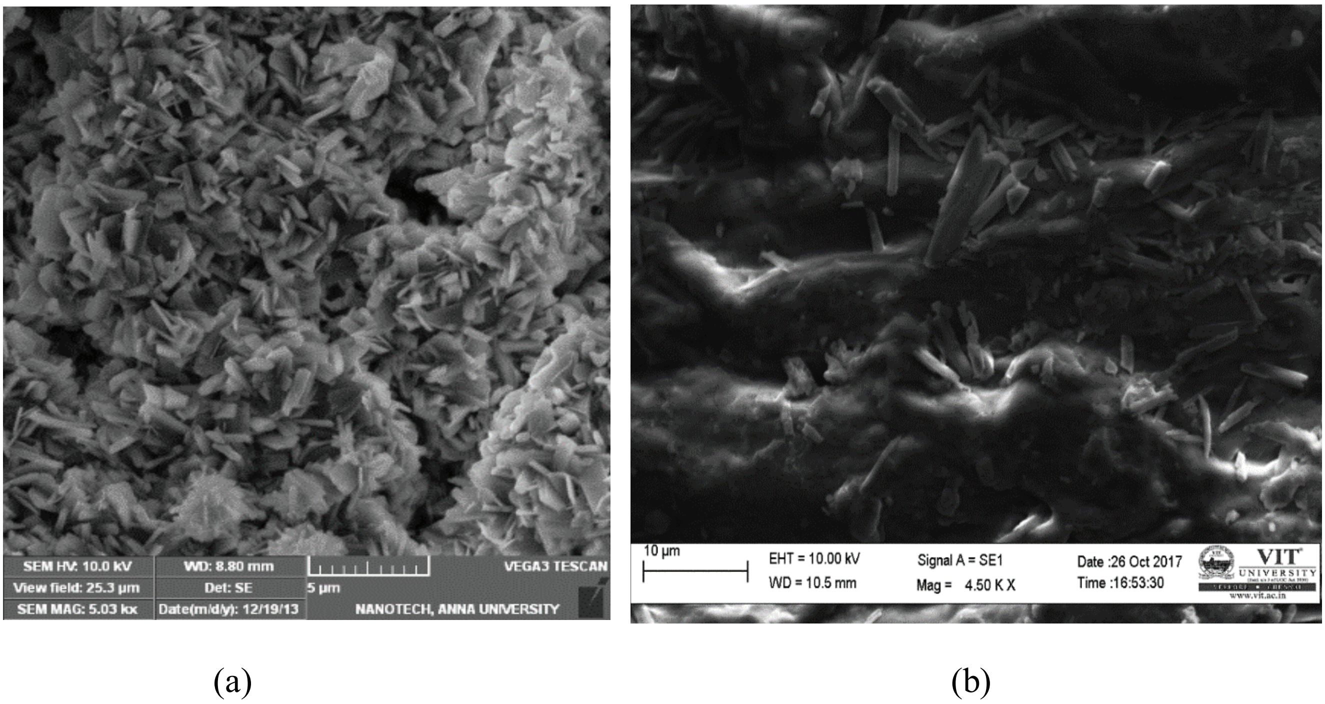

Fig. 1. SEM image of (a) raw alginate and (b) Reactive Magenta dye-loaded alginate after coagulation.

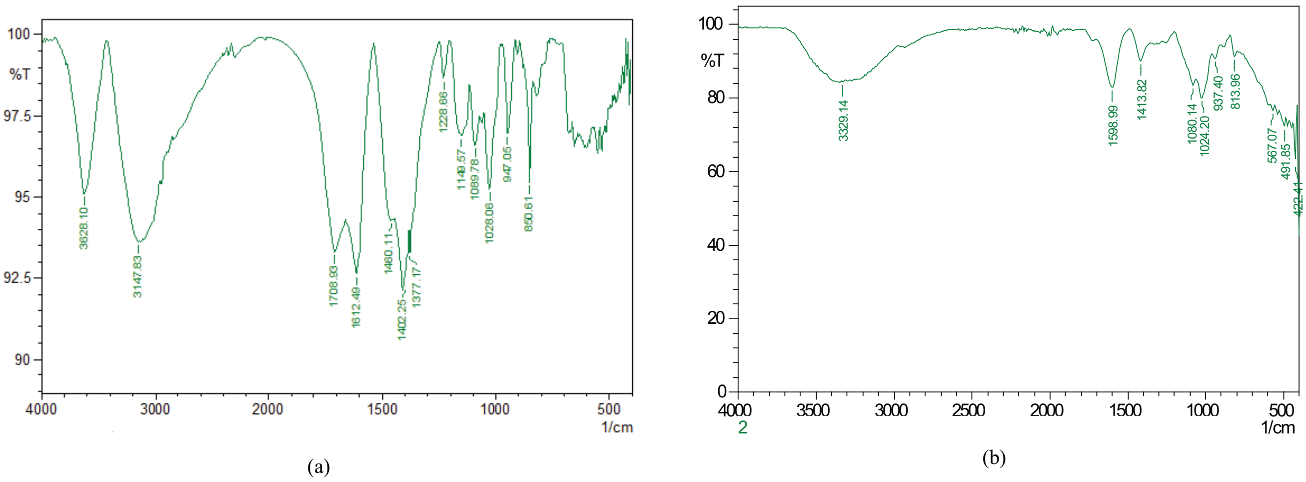

Fig. 2. FTIR spectra of (a) raw alginate and (b) Reactive Magenta dye-loaded alginate after coagulation.

was studied, and the results are presented in Fig. 3. For real effluent containing Reactive Magenta, the maximum color removal of 92.7% was attained at 4 g/L of calcium dose and 30 mg/L of alginate dose. It was observed during the experiments that the calcium alginate gel formation was not appropriate at low-calcium doses. The optimum condition for maximum color removal is shown in Table 4.

3.4. Effect of settling time

The settling time is one of the operating parameters during the coagulation process. For the optimum condition for Reactive Magenta dye removal in textile waste water given in Table 4, the experiments were carried out up to 60 min. Fig. 4 shows the effect of settling time on percentage color removal. It can be observed from the figure that there is a consistent increase in color removal with increase in settling time. The optimum settling time and maximum color removal was found to be 50 min and 92.7%.

4. Coagulation mechanism

The classic coagulation process will follow any one of the following mechanisms [23]: (a) double layer compression, (b) sweep flocculation, (c) adsorption and charge neutralization, and (d) adsorption and interparticle bridging. In the case of natural polymers such as alginate, it may generally follow the mechanism (d). During the coagulation of very long polymer chain of alginate molecules on the surface of particles, they may form loops. At the end of these loops, it may attach with another particle and forms a bridge between the two particles, which is known as the bridging mechanism of flocculation. The charges of particles and polymers do not play any important role in this mechanism [24].

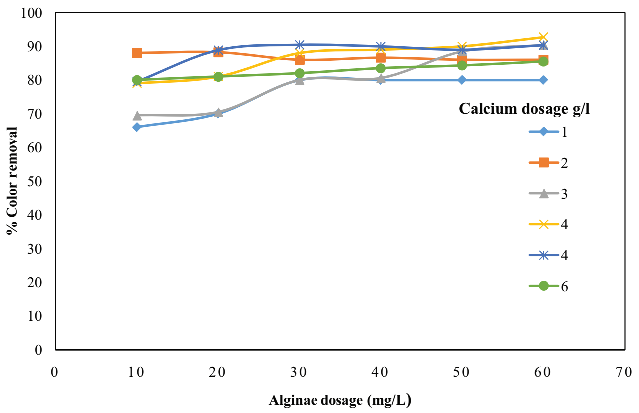

Fig. 3. Effect of calcium and alginate dose on initial dye concentration on the removal of Reactive Magenta dye.

The coagulation process can be enhanced by any one of the mechanisms: charge neutralization along with bridging the 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; when natural long chain polysaccharides interacted with divalent cations such as Ca^{2+}, it forms an egg box structure which leads to stable gel formations [6,11]. The nest-like sites in the two consecutive chains will accommodate the Ca^{2+} ions. This study follows the above mechanism.

5. Conclusion

The optimum condition for removal of Reactive Magenta dye in real-time textile effluent by an alginate as a coagulant extracted from *Sargassum* sp. was investigated. The maximum color removal of 92.7% was found to be at 30 mg/L of alginate dose, 4 g/L of calcium dose, and 50 min of settling time for the pH of 7. During the color removal process, the free calcium ions boosted the gel formation with the alginate and at lower doses of calcium, the gel formation is not sufficient to remove the dye. It can be observed that there is a steady increase in color removal with increase in settling time. The obtained results reveal that the alginate will be an effective coagulant for the removal of Reactive Magenta dye in textile effluent.

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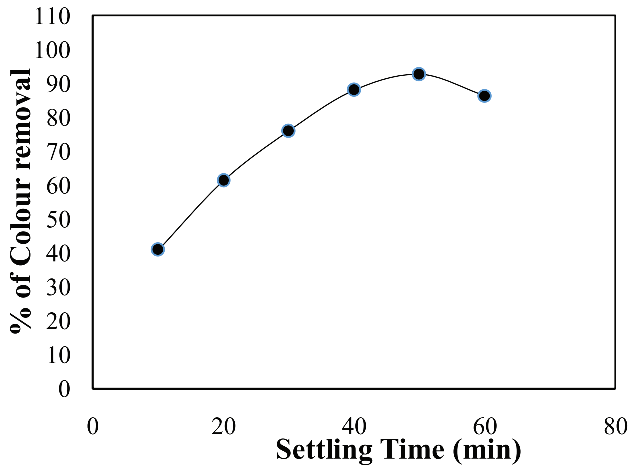

Fig. 4. Effect of settling time on percentage dye removal.

Table 4
Optimum condition for maximum color removal

Dye	pH	Initial dye concentration (mg/L)	Alginate dose (mg/L)	Calcium dose (g/L)	Dye removal (%)
Real-time effluent containing Reactive Magenta dye	7	100 color units	30	4	92.7

Note: The bold value represents the optimum percentage colour removal.

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