Effective Removal of Acid Black 1 Dye in Textile Effluent Using Alginate from Brown Algae as a Coagulant

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ABSTRACT *In this study, the Acid Black 1 dye containing effluent collected from a dyeing unit was examined with the alginate extracted from the marine brown algae, Sargassum sp. for its removal. Batch experiments were carried out using standard Jar test apparatus. Fourier Transform InfraRed (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM) techniques were used to characterize the raw alginate and dye loaded alginate after the coagulation process. The optimum condition for maximum colour removal of 96.8 % was found to be at 40mg/L of alginate dose, 6g/L of calcium dose and 30 minutes of settling time for the pH of 4.2. The experimental data were analyzed with the first and second order kinetic model and kinetic study on the coagulation process reveals that it follows second order kinetic model. The results revealed that alginate extracted from marine brown algae Sargassum sp has the coagulation potential for effective removal of Acid Black 1 dye.*

KEYWORDS: *Acid Black 1 Dye; Marine brown algae; Coagulation; Kinetics.*

INTRODUCTION

Synthetic dyes are widely used in various process industries like textile, paper, printing and other allied industries. It was reported that around 7×10^5 tonnes of dye produced per year which forms a large and important group of water pollutants in an aquatic ecosystem [1]. Among those synthetic dyes, Azo dyes, which contain one or more azo bonds, are the most widely used synthetic dyes and these azo dyes are the major pollutant in dye wastewater. Due to their toxicity and slow degradation, these dyes are classified as environmentally hazardous materials [2]. The Central Pollution Control Board of India has listed these dye and dye intermediate industries as one among the most heavily polluting industries [3]. The hazardous nature of dyes can create activity. Dermatitis is the adverse effects of these dyes. The pollution problem becomes more severe in developing countries like India where rapid population growth and industrialization has increased the complexity of industrial effluents. Hence, the proper treatment of textile industry effluent for the effective removal of dye becomes essential [4]. A variety of physicochemical methods such as biological, adsorption, membrane, coagulation & flocculation, oxidation-ozonation, and Advanced Oxidation Processes (AOPs) has been generally used for the treatment of textile effluents [5]. Coagulation is one of the most economical physicochemical methods used to remove the colour in industrial wastewater containing synthetic dyes. The performance of

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1021-9986/2018/4/145-151 7/$/5.07

the coagulation process is purely dependent on the type of coagulant used [6]. Coagulants used for water and wastewater treatment are predominantly inorganic salts of iron and aluminum which causes the formation of a large quantity of sludge possesses toxicity and causes various adverse effects like Alzheimer's disease due to high doses of Alum [7-9]. To overcome these negative impacts it is mandatory to look for an alternate low cost coagulant, and this can be well satisfied by the natural bio polymer alginate which is available plenty in marine brown algae Sargassum sp. Alginate is located in the cell wall and in the matrix of the algae, cementing the cells together and giving certain mechanical properties to the algae. Alginate is a linear, anionic polysaccharide with an abundance of free hydroxyl and carboxyl groups distributed along the polymer chain backbone [10]. The unique nature of alginate is to have a carboxyl group which has the ability to form a strong insoluble gel so called "egg-box" structure during the reaction with metal cations like calcium [11,12]. This gel formation property enables the alginate to act as an effective coagulant. The main objective of this study is to assess the coagulation potential of alginate extracted from marine brown algae Sargassum sp. for the removal of Acid Black 1 dye from textile effluent.

EXPERIMENTAL SECTION

Sample collection

The sample (effluent containing Acid Black 1 dye) used in this study was collected from the local fiber dyeing unit located at Kanchipuram District of Tamil Nadu State in India. The effluent from the dye bath mainly contains Acid Black 1 dye and the characteristics are presented in Table 1. Acid black 1 dye is the anionic azo dye having a molecular weight of 616.49g/mol [13]. The molecular structure of Acid black 1 dye is shown in Fig. 1 [14] and the physiochemical properties of Acid Black 1 dye are presented in Table 2 [5].

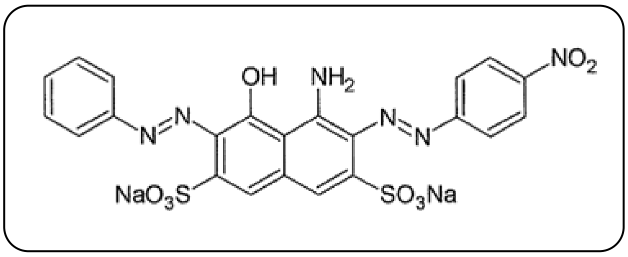

Fig. 1: Molecular Structure of Acid Black 1.

Algae collection

Brown algae (*Sargassum sp)* were collected from coastal waters (Bay of Bengal) of Mandapam (9.27° N 79.12° E), Tamil Nadu, India during January 2015. Collection of samples was done by cutting the thallus with a knife near the rizoid. 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 sample was washed abundantly with tap water and dried for 30 hours at 65°C. Alginate extraction from algae was carried out based on the procedure reported by *Fenoradosoa et al.,* 2010 [15]. 25 g of dried algae were soaked in 800mL of 2% formaldehyde for 24 hours at room temperature, washed with water after which soaked with 800mL of 0.2M HCl for 24 hours. Later, 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%. Sodium alginate collected was washed twice by 100mL of acetone, dried at 65°C and dissolved in 100mL of distilled water. It was then precipitated again with ethanol (v/3v) and dried at 65°C.

Characterization of Alginate

Fourier Transform InfraRed (FT-IR) spectroscopy and Scanning Electron Microscopy (SEM) techniques were used to characterize the raw and dye loaded alginate samples. The FT-IR spectroscopy (Thermo Nicolet, AVATAR 330) was employed to determine the functional groups present in the alginate. The infrared spectrum of alginate was recorded as KBr discs in the range of 4000-400 cm^{-1}. Scanning Electron Microscopy (TESCAN, VEGA 3 & ZEISS) was used to characterize the surface structure and morphology of the raw and dye loaded samples of alginate.

Experimental Procedure

The coagulation test was carried out in a standard jar test apparatus using alginate as a coagulant for removal of Acid black 1 dye from a dye bath solution. The experiments were conducted in 1L glass beakers containing 500ml of dye waste water of initial dye concentration 1000mg/L. Calcium as calcium chloride

Table 1: Characteristics of dye effluent.

Parameter	Concentration
The concentration of Acid black 1 dye	1000ppm
pH	4.2
Absorbance	618nm
Temperature	30 °C

Table 2: Physicochemical properties of the Acid Black 1.

Parameter	Values
Molecular weight	616.49g/mol
Molecular formula	$C_{22}H_{14}N_6Na_2O_9S_2$
Absorption maxima	618nm
Color	Dark blue black
Colour index number	20470
Dye class	Diazo
Solubility	3 % in water

and alginate as extracted algal sodium alginate were used for the experiment. The calcium dose varied between 1 to 6g/L, whereas the alginate dose varied between 10 to 60mg/L. Calcium was added first and then alginate was added for all the experiments. The experiment for each sample was carried out in the following order: 5 minutes flash mixing at 100rpm for calcium dosing, 5 minutes rapid mixing at 100rpm for alginate dosing, followed by 20 minutes slow mixing at 40rpm and 30 minutes for settling. The supernatant after sedimentation was filtered using Whatman no. 42 filter paper and the filtrate was analyzed using UV-spectrophotometer (Systronics-119, India). The percentage of dye removal was calculated by using equation (1).

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

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

RESULTS AND DISCUSSION

SEM Analysis

The morphology of the alginate surface (before and after the coagulation) is depicted in Fig. 2(a-b). It can be noted from the figure that the surface of alginate before the coagulation process (Fig. 2a) possess flaky spines like structure and fine perforations on it. Further, it can also be noted that after coagulation process (Fig. 2b), the surface of the sample becomes smooth and no flakes were found which could be due to the binding of Acid Black1 dye particles on to the gel formed by calcium and alginate. The morphological change in the surface of the alginate reveals the removal of dye through the coagulation process.

FT-IR Analysis

The FTIR spectrum of raw and dye loaded alginate are presented in Fig. 3. It can be noted from Fig. 3a (raw alginate) that a broad band at 3147cm^{-1} and 3628cm^{-1} was assigned to hydrogen bonded O-H group. A sharp and strong absorption bond at 1612cm^{-1} representing the C=C stretch [16]. The band at 1460cm^{-1} indicates the methylene C-H stretch [17]. A major band in the region 1708cm^{-1} and 1612cm^{-1} indicate the presence of a C=O group (carbonyl group) and this confirms the nature of alginate [15]. Fig. 3b represents the FT-IR spectrum of sludge containing alginate and Acid black 1 dye. A broad band between 1367cm^{-1} and 1739cm^{-1}represents the open chain azo group which is due to the presence of Acid black 1 dye in the sludge [18]. A short stretch at 2970cm^{-1} indicates the presence of $-CH_3$ group and a band starts from 1708cm^{-1} in Fig. 3a was shifted to 1739cm^{-1} in Fig. 3b because of the influence of the azo group in C=O group. A narrow peak from 1228 – 1215cm^{-1} in Fig. 3b represents the presence of aromatic primary amine C-N stretch due to the combination of C=O group present in alginate and azo group present in the acid black 1 dye.

Effect of Calcium and Alginate dose

The effect of calcium and alginate dose on the removal of Acid black 1 dye in the effluent is presented in Fig. 4. It can be observed from the figure that the percentage of dye removal increases with an increase in alginate dose for all calcium doses. Initially the concentration of Acid black 1 in textile dye was found to be 1000mg/L, by changing the calcium and alginate dose, the percentage of dye removal varies from 65% to 96%. The maximum colour removal of 96.8% was attained at 6g/L of calcium dose and 40mg/L of alginate dose. During the colour removal process the role of calcium is very vital as the free calcium ions enhance the gel

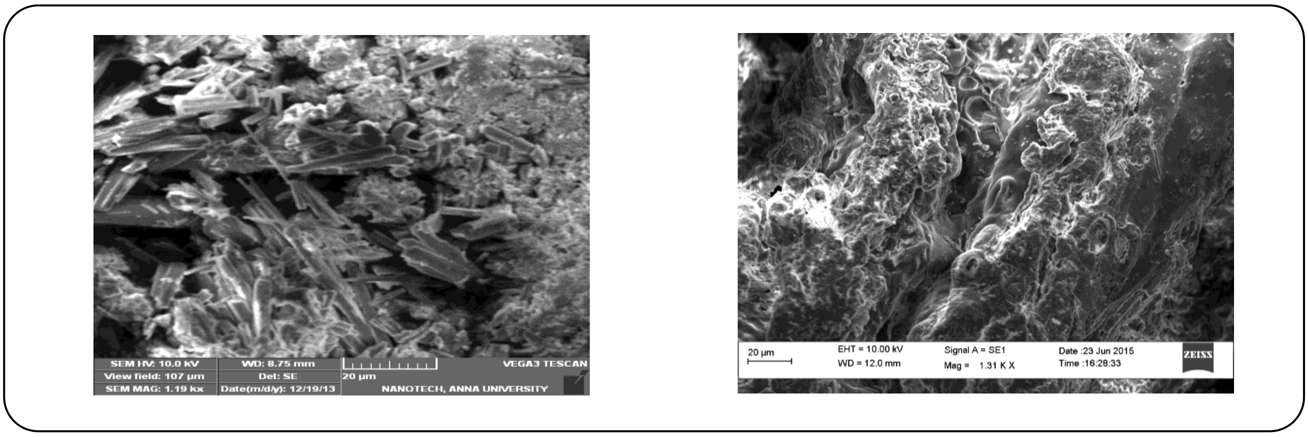

Fig. 2: SEM image of alginate (a) raw and (b) after coagulation.

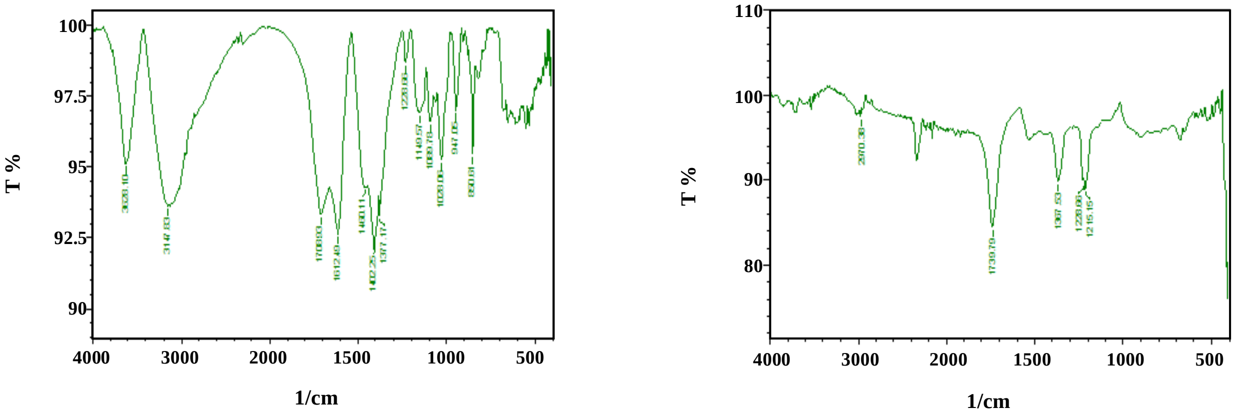

Fig. 3: FT-IR spectra of raw (a) and dye loaded alginate (b).

formation with the alginate and thereby free settling occurs and the effective coagulation was achieved. At lower doses of calcium, the gel formation is not sufficient to remove the dye dispersed in the textile effluent.

Effect of Settling Time

The settling time is one of the operating parameters during the coagulation process. Fig. 5 shows the effect of settling time on percentage colour removal. It can be observed from Fig. 5 that there is a consistent increase in colour removal with an increase in settling time. The optimum settling time and maximum colour removal were found to be 30 minutes and 96.8 %.

Coagulation Kinetics

The coagulation kinetics for the removal of Acid black 1 dye in the textile effluent using alginate as a coagulant was studied. The rate of removal of dye in the coagulation process is proportional to the initial dye concentration and formation of calcium alginate complex. First order and second order rate equation were verified with the experimental data [19]. The solution for the first order equation is given in Equation (2)

$$\log\left(\frac{C_i}{C_0}\right) = -kt \tag{2}$$

Where *Ci* is initial dye concentration,

C_0 is the 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 (3)

$$\frac{1}{C_o} - \frac{1}{C_i} = k't \tag{3}$$

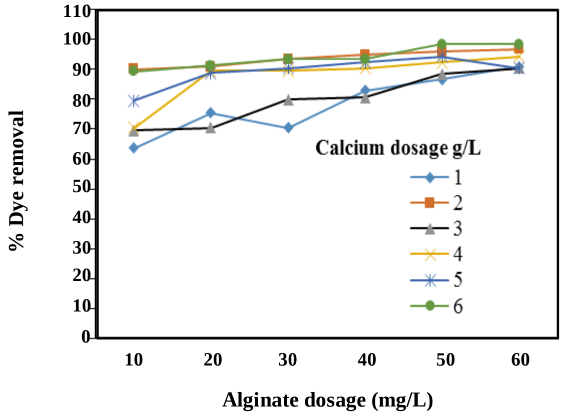

Fig. 4: Effect of calcium and alginate dose on percentage dye removal.

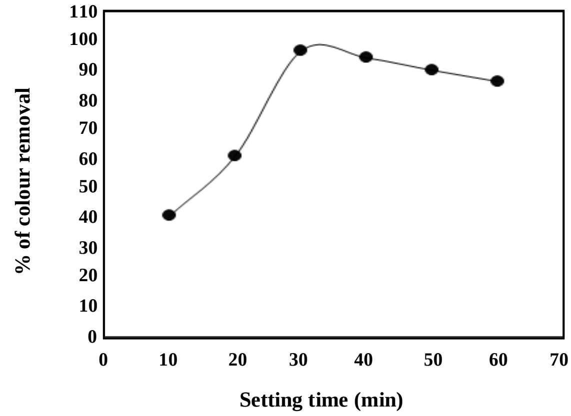

Fig. 5: Effect of Settling Time on percentage dye removal.

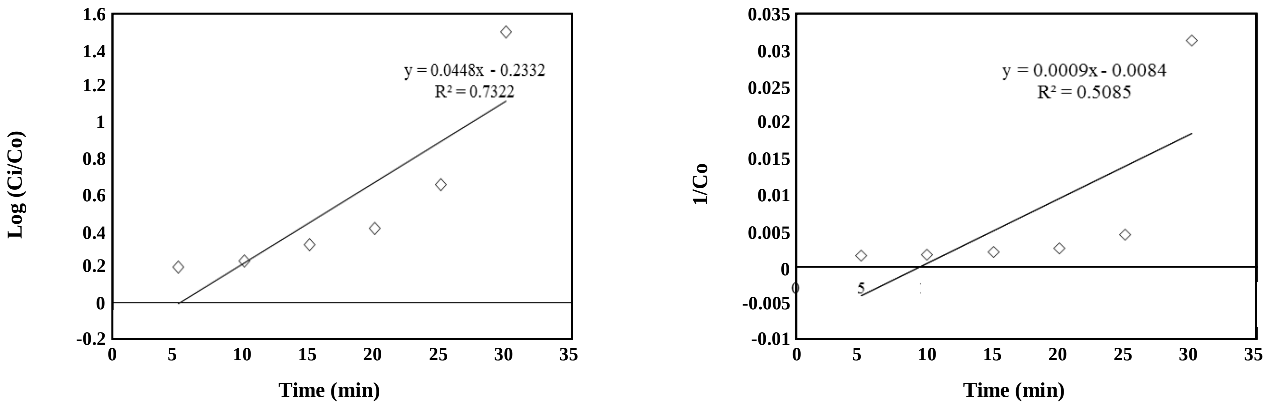

Fig. 6: Coagulation kinetics plot for (a) First order (b) Second order rate equation.

Where *k'* is the second order rate constant (L / mg min)

The plots for the first order and second order kinetics to the experimental data with various initial dye, concentrations are presented Figs. 6 (a) and 6 (b) respectively. It can be noted from these figures that the first order equation showed a 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 Acid black 1 dye solution using algal alginate followed second order kinetics [19].

Coagulation Mechanism

Generally, the coagulation process may follow any one of the following mechanisms: (a) Double layer compression; (b) Sweep flocculation; (c) Adsorption and charge neutralization; (d) Adsorption and interparticle bridging [20]. For natural polymers like alginate, Adsorption and interparticle bridging mechanism may dominate. Looping of the very long polymer chain of alginate molecules on the surface of particles may occur and these loops 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 [21]. The coagulation process can be enhanced by any one of the mechanism: 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 [22]. *Grant et al.* [23] reported that when natural long-chain polysaccharides interacted with divalent cations like Ca, it forms an egg box structure which leads to stable gel formations. The nest like sites in the two consecutive chains will accommodate the Ca ions. The above mechanism is applicable to the present study.

CONCLUSIONS

The coagulation potential of alginate extracted from brown algae, *Sargassum sp* for the removal of Acid black 1 dye in textile effluent was studied. The optimum condition for maximum colour removal of 96.8 % was found to be at 40mg/L of alginate dose, 6g/L of calcium dose and 30 minutes of settling time for the pH of 4.2. During the colour removal process, the free calcium ions enhanced the gel formation with the alginate. SEM images and FT-IR analysis confirms the changes in morphology and functional group of the alginate due to binding of dye on it during coagulation. The kinetic study on coagulation reveals that the process follows second order kinetics. Based on the experimental results, it is evident that alginate extracted from the marine brown algae will be an effective coagulant for the removal of Acid Black 1 dye.

Acknowledgement

The authors would like to thank VIT University, Vellore, India for providing the necessary facility to carry out this research work.

Received: Jul. 13, 2016 ; Accepted : Dec. 12, 2017

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