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TREATMENT OF REACTIVE DYE CONTAINING TEXTILE WASTEWATER USING MICROWAVE ASSISTED SYNTHESIZED POLY(DIALLYLDIMETHYL AMMONIUM CHLORIDE)

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ABSTRACT

Results on the applicability of microwave assisted synthesized poly(diallyldimethyl ammonium chloride) (polyDADMAC) in reactive dye containing textile wastewater treatment are reported. Diallyldimethylammonium chloride and poly(diallyldimethylammonium chloride) have been characterized by spectral means. The microwave assisted synthesized polyDADMAC has shown some effectiveness in textile wastewater treatment. COD removal efficiency of actual textile wastewater is below 30% whereas the standard dye sample shows about 50-60% COD removal efficiency. TDS and TSS also decreased after treatment of the wastewater with polyDADMAC.

Key words: Wastewater treatment, Poly(diallyldimethylammonium chloride), Biochemical oxygen demand (BOD), Chemical oxygen demand (COD) and dyes

INTRODUCTION

Textile and dyeing industry use different kinds of dyes and direct discharge of colored wastewater into lakes and rivers is harmful for aquatic life (Teh *et al*. 2016, Verma *et al*. 2012). Different types of chemicals are used during different stages of processing. These include strong acids, strong alkalis, sodium hypochlorite, dyes, bleaching agent, starch, thickening agent, softeners, acetic acid, wetting and dispensing agents. Wastewater containing these toxic effluents must be removed before discharge as they increase biochemical oxygen demand (BOD), chemical oxygen demand (COD), solid contents and toxicity. Among various dyes, textile industries frequently use reactive azo dyes. Carcinogenic products such as aromatic amines are produced from azo dyes (Yahagi *et al*. 1975). Aminoazo benzene dyes may lead to mutagenesis and can cause cancer (Garg *et al*. 2002).

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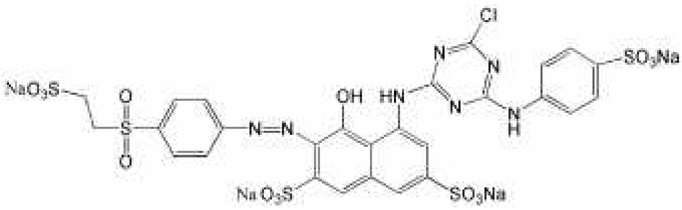
Both biological and chemical treatments are frequently used for textile wastewater treatment. Biological process is effective in BOD and suspended solids (SS) removal but inefficient for color removal. In this respect, coagulation-flocculation is the most economic and efficient method in removing color from waste water (Bidhendi *et al.* 2007, Robinson *et al.* 2001). Flocculating agent destabilizes the colloidal particles charges and allows the particles to agglomerate into larger settleable flocs (Lee *et al.* 2014). Flocculating agents can be divided into two categories: inorganic and polymeric. The common inorganic flocculants are alum [$Al_2(SO_4)_3.18H_2O$], lime [$Ca(OH)_2$], ferric chloride ($FeCl_3.6H_2O$), ferrous sulphate ($FeSO_4.7H_2O$) and $MgCl_2$. Polymeric materials used as flocculants are mostly water-soluble linear polymers. These polymers can be cationic, anionic or nonionic type. Polymeric materials possess more advantages than inorganic coagulants. Polymeric flocculants has the ability to produce large, dense, compact and stronger flocs with good settling power than the inorganic coagulants. It also reduces the sludge volume significantly. Moreover, polymers require lower doses. With polymers, there is an overall reduction in treatment costs. Savings originate from reduced chemical costs and lower maintenance costs due to the mild nature of the polymers. The inorganic coagulants are aggressive and highly corrosive chemicals. Among various polymeric flocculants, poly(diallyldimethylammonium chloride), epichlorohydrin-dimethylamine (EPI-DMA) and polyacrylamide are mostly used in wastewater treatment (Oladoja 2016, Villalobos *et al.* 2016). The remarkable feature of polyDADMAC is that it is cationic and highly soluble in water (Lee *et al.* 2014). Recently, ultra high molecular weight poly (dimethyldiallylammonium chloride) has also been developed (Zhang *et al.* 2016). Razali *et al.* treated pulp and paper mill wastewater with different molecular weight polyDADMAC and found that higher molecular weight polyDADMAC was more effective in flocculation compared with lower molecular weight polyDADMAC (Razali *et al.* 2011). Moreover, quaternary ammonium salt-based polymeric composite (Gupta *et al.* 2016) and inorganic-organic hybrid polymer (Yeap *et al.* 2014) have also been developed for the treatment of textile wastewater.

The objective of this study is to investigate the applicability of polyDADMAC in the treatment of reactive dye containing textile wastewater.

MATERIALS AND METHODS

Dimethylamine, allyl chloride, ammonium persulfate, sodium thiosulfate, ferrous ammonium sulfate, magnesium sulfate, sodium hydroxide, potassium dichromate, ferric chloride, acetone, methanol, EDTA, hydrochloric acid were purchased from Sigma Aldrich, Germany. Allyl chloride was distilled before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER 400MHz NMR spectrometer. The infrared spectra were recorded on KBr pellets with a SHIMADZU IR spectrometer. The polyDADMAC has been synthesized using a domestic microwave (Brand: Miyako) according to a literature procedure (Bing-hui *et al.* 2005). The irradiation power of microwave is 75-750 W. A 250 mL round bottom flask containing the reaction mixture was placed inside the microwave oven and a reflux condenser was connected with it. The mixture was heated under microwave irradiation. BOD, COD and DO of samples were measured by adopting the standard methods (Michael *et al.* 1975). Textile wastewater samples were collected from NAZ Bangladesh Ltd., Tusuka Processing Ltd., Meghna Knit Composite Ltd., Zaintex Composite Ltd., and DIRD Composite Textiles Ltd. (unit-02) of Gazipur, Bangladesh. About 2.0 L textile wastewater samples were collected in plastic containers. Each plastic container was washed with dilute HNO_3 before use. In the present study Remazol red RR, Remazol yellow RR, and Remazol blue RR reactive dyes were used for investigating their removal with polyDADMAC.



Remazol Red RR.

Microwave assisted synthesis of diallyldimethylammonium chloride (DADMAC) (**1**)

Dimethylamine $(CH_3)_2NH$ (26.76 mL, 0.1 mol) and allyl chloride C_3H_5Cl (15.306 mL, 0.1 mol) were mixed in a 250 mL round bottom flask, stirred, and cooled to 5°C. Then sodium hydroxide (8 g, 0.1mol) was added to the reaction mixture. The temperature of the reaction mixture was kept below10°C. The reaction mixture was refluxed under microwave irradiation for 1 hour and temperature varied from 45°C to 60°C. After 1 h of reflux, the mixture was transferred into a separatory funnel for filtration at room temperature. An oily layer and aqueous layer were formed. The aqueous layer was found at the bottom. The oily layer was found in the upper part and separated out in a round bottom flask and allylchloride (15.3 mL, 0.1 mol)) was added to it. Then 5% HCl acid was added to adjust the pH at 4.5-7. The reaction mixture was refluxed again for 1 hour. After reflux, the oily part was separated and washed with acetone and solvent was removed by rotary evaporator to get DADMAC. Yield: 75%. ^1H NMR ($CDCl_3$, 400 MHz, 25°C, δ ppm): 3.3 (s, 3H), 4.2 (d, 2H), 5.7-5.9 (m, 2H), 6 (m, 1H). $^{13}C\{1H\}$NMR ($CDCl_3$, 100 MHz, 25°C, δ ppm): 49.70 ($-CH_3$), 65.78 ($-CH_2-$), 124.48 (-CH=), 129.94 ($CH_2=$). FTIR (υ/cm^{-1}): υ(CH_2=CH, out of plane bending) 848.66-952.84; υ(C-N stretching) 1107.14-1220.84; υ(^{sp3}C-H bending) 1423.47-1481.33;

υ(C = C stretching and H-O-H bending) 1641.42; υ(^{sp3}C-H stretching) 2970.36; υ(C-H stretch of C = C-H) 3012.81.

Microwave assisted synthesis of poly(*diallyldimethylammoniumchloride*) (polyDADMAC) (**2**)

Diallyldimethylammonium chloride (DADMAC) (2.0 g) was dissolved in 15 mL water in a 250 mL three necked flask and kept in a hot water bath at 60°C with stirring. Nitrogen gas was passed into the flask for an inert atmosphere and ammonium persulfate (1.3 g) and sodium thiosulfate (0.4 g) were added into flask simultaneously. The mixture was refluxed at 60°C for 1.5 hours under microwave irradiation. The crude polyDADMAC was washed with acetone (10 mL) and absolute alcohol and then the solvent was removed with rotary evaporator at 65°C and dried. The obtained polyDADMAC is colorless viscous. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C, δ ppm): δ 1.7 (d, 2H), 2.3 (m, 1H), δ 3.3 (s, 3H), 4.0 (d, 2H).^{13}C{1H}NMR ($CDCl_3$, 100 MHz, 25°C, δ ppm): δ 25 (-CH_2-), 39 (-CH-), 52 (N-CH_3), 70 (N-CH_2-). FTIR (υ/cm^{-1}): υ (C-N stretching) 1045.42-1257.59; υ(^{sp3}C-H bending of methyl) 1317.38-1525.69; υ(H-O-H bending) 1637.56; υ(^{sp3}C-H stretching) 2823.79-2881.65; υ(H-O-H stretch) 3360.

Flocculation test

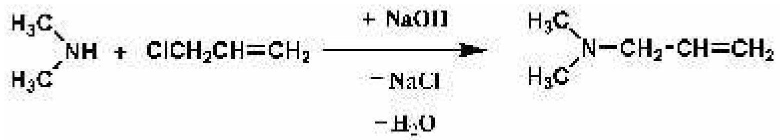
Jar test was performed for flocculation test. 1.0 L textile wastewater was transferred to a beaker under starring. The flocculating experiment was conducted at room temperature. After being dosed with 0.2 – 1 ppm of polyDADMAC, it was stirred and the flocs were allowed to settle.

RESULTS AND DISCUSSION

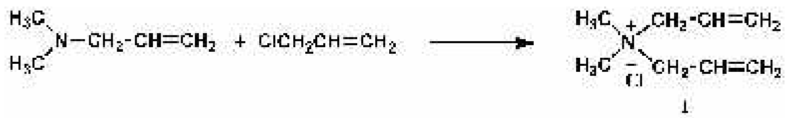
Synthesis and characterization

Diallyldimethylammonium chloride (DADMAC, **1**) was prepared by two step process (Bing-hui *et al*. 2005). The first step is the alkylation of dimethylamine with allyl chloride in an aqueous alkaline medium. This step is followed by a quaternization in an organic medium again with another mole of allyl chloride.

1st step: Synthesis of allyldimethylamine



2^{nd} step: Quaternization of allyldimethylamine to produce DADMAC



Synthesis of diallyldimethylammonium chloride.

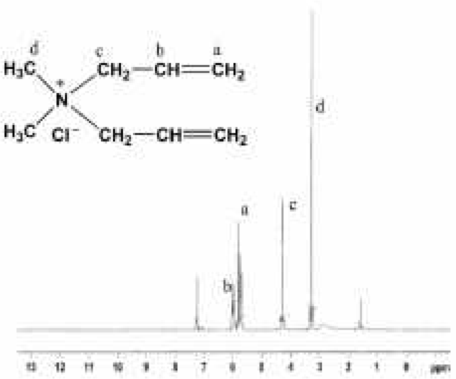


Fig. 1. ^{1}H NMR spectrum of DADMAC.

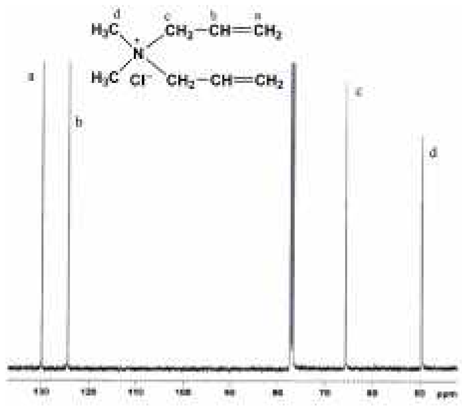


Fig. 2. ^{13}C NMR spectrum of DADMAC.

The ^{1}H NMR spectrum of DADMAC (Fig. 1) shows a peak at δ 3.3 assigned to the absorption of $–CH_3$ linked with N, doublet peak at 4.2 ppm is due to $–CH_2$-, multiplet at 5.7-5.9 is attributed to $=CH_2$ group of $–CH=CH_2$ and multiplet at 6 ppm is due to –CH= group of $–CH=CH_2$.

The ^{13}C NMR spectrum of DADMAC (Fig. 2) shows peaks at δ 49.70, 65.78, 124.48, 129.94, which are attributed to the absorption of carbon atoms in $–CH_3$, $-CH_2$-, -CH=, and CH_2= in DADMAC monomer, respectively. FTIR (υ/cm^{-1}) of DADMAC monomer shows a strong and broad absorption peak at 3375.43 cm^{-1}, which arises for stretching vibration of –OH of water due to strong hygroscopic nature of DADMAC. The other major bands are as follows: the bands from 848.66 - 952.84 cm^{-1} are due to C-H out of plane bending from CH_2 = CH-. The C-N stretching is at 1107.14 – 1220.84 cm^{-1}. The bands from 1423.47 – 1481.33 cm^{-1} arises from ^{sp3}C-H bending. The peak at 1641.42 cm^{-1} is the characteristic stretching band of C=C. The peak at 2970.36 is attributed to ^{sp3}C-H stretching. The C-H stretch of C = C-H is at 3012.81 cm^{-1}.

Traditionally, poly(DADMAC) is synthesized by free radical polymerization process initiated mostly by persulfate initiator using an aqueous solution of the diallyldimethylammonium chloride (DADMAC) monomer. In this process, the reaction mixture requires at least five hours reflux to complete the polymerization reaction to obtain average molecular weight between 400,000 and 500,000 Da. In this study, poly(DADMAC) has been synthesized under microwave irradiation for 1.5 h by reacting DADMAC monomer with ammonium persulfate and sodium thiosulfate in an inert atmosphere. The produced polymer is colorless viscous. Microwave assisted method requires less time compared to the traditional method to produce the polymer.

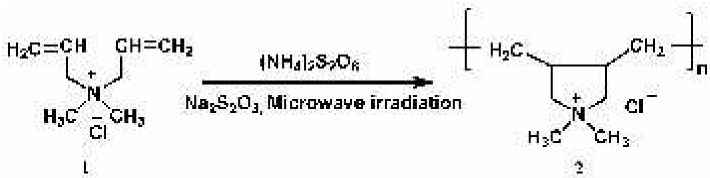


Fig. 3. Synthesis of polyDADMAC.

The [1]H NMR spectrum of polyDADMAC (Fig. 4) shows a peak δ 1.7 due to absorption of –CH_2- in the main chain. The peak at δ 2.3 is assigned to the absorption of –CH- in the polymeric five member ring. The peak at δ 3.3 is due to the –CH_3 linking with N. The peak at δ 4.0 is attributed to the absorption of –CH_2- linking with N. The disappearance of peaks at δ 5.7-5.9 and 6 ppm in the [1]HNMR spectrum of polyDADMAC shows the proof of the complete polymerization of DADMAC monomer.

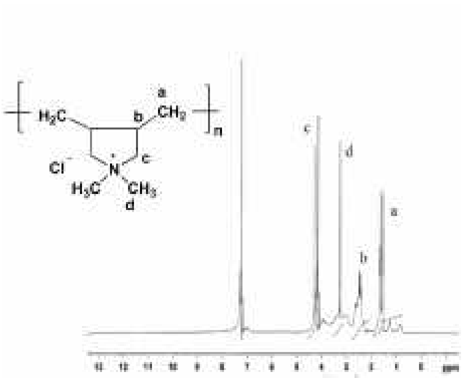


Fig. 4. [1]H NMR spectrum of polyDADMAC.

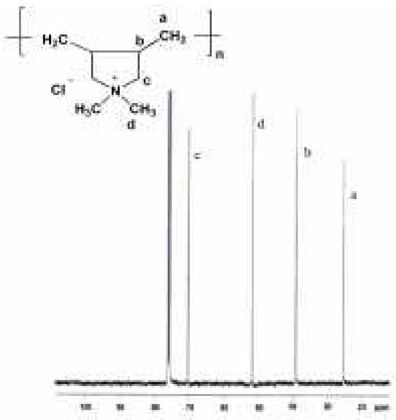


Fig. 5. [13]C NMR spectrum of polyDADMAC.

The [13]C NMR spectrum of polyDADMAC (Fig. 5) shows the peak at δ 25 attributed to the absorption of –CH_2- in the polymer chain. The peak at δ 39 is due to –CH- of the five member ring of the polymer. The peak at δ 52 is assigned to N-CH_3 and peak at δ 70 is for N-CH_2- on the five member ring in the polymer. The peaks at δ 124.48 and 129.94 assigned to the carbon atoms in double bonds disappeared in [13]C NMR spectrum of the polymer also indicates that the polymerization of DADMAC were complete.

In the FTIR (υ/cm^{-1}) of polyDADMAC (Fig. 6), there is no band at 848.66 - 952.84 cm^{-1} which arise due to C-H out of plane bending from CH_2=CH-. The C-H stretch of C = C-H is also absent at 3012.81 cm^{-1}. This indicates that the monomer has completely polymerized. Since both peaks of $\upsilon_{c=c}$ and υ_{H2O} appear at 1637 cm^{-1}, they could not be used as a tool to proof the existence of double bond in the polyDADMAC. The peak at 3360 cm^{-1} is due to OH stretch of water as the polyDADMAC is synthesized in water and it is a viscous liquid. The C-N stretch is at 1045.42-1257.59 cm^{-1}, sp^3C-H bending of methyl is at 1317.38-1525.69 cm^{-1} and sp^3C-H stretching of methylene (-CH_2-) is at 2823.79-2881.65 cm^{-1} .

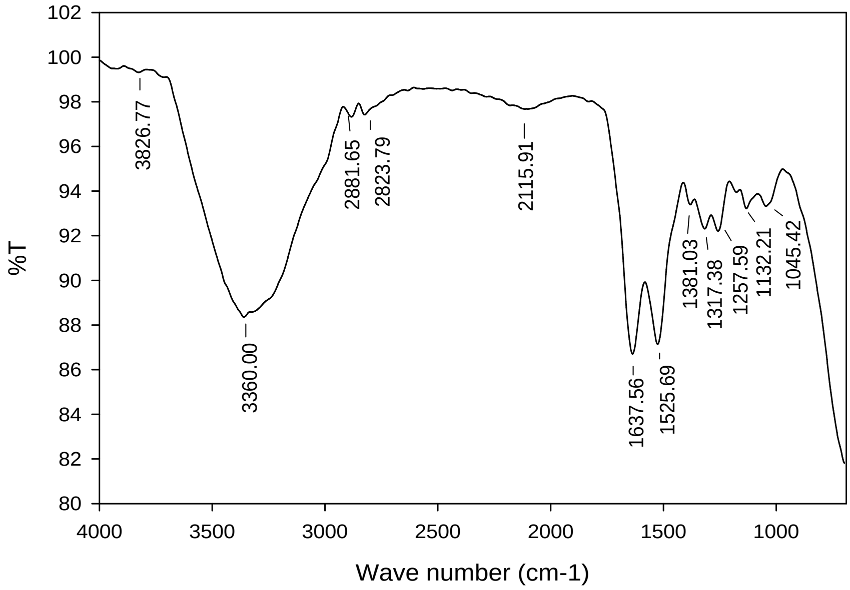


Fig. 6. FTIR of polyDADMAC.

Flocculation test by polyDADMAC

The produced polyDADMAC was used for treatment of standard reactive dye and actual wastewater samples from textile industries. Table 1 shows the permissible limit of various water quality parameters of Bangladesh standard.

Table 1. Permissible limit of water quality parameters.

Water Quality Parameters	Bangladesh Standard
pH	6.5-9
BOD	50 (mg/L)
COD	200 (mg/L)
DO	4.5-8 (mg/L)
TDS	2100 (mg/L)
TSS	150 (mg/L)

Standard reactive dye solution was prepared (1 mg/L) and was treated with 0.2 -1 ppm polyDADMAC (Table 2). COD removal efficiency (CRE) was calculated according to the equation 1.

$$\text{COD removal efficiency (CRE)} = \frac{D_0 - D}{D_0} \times 100 \qquad ..... (1)$$

where, D_0 = COD value before treatment

D = COD value after treatment

It is found that COD removal efficiency of remazol red, remazol yellow and remazol blue is 50.90, 55.55 and 65.87%. After treatment, the BOD_5 value decreases and dissolved oxygen (DO) increases in the samples.

Table 2. PolyDADMAC treatment of various standard dye samples.

Reactive Dye	Treatment Condition	pH	BOD_5 (mg/L)	COD (mg/L)	DO (mg/L)	TDS (mg/L)	TSS (mg/L)
Remazol red RR	Before	6.63	105	277	3.01	175	87
	After	6.33	21	136	4.00	169	56
Remazol yellow RR	Before	6.30	173	333	2.72	182	96
	After	6.20	47	148	3.90	174	73
Remazol blue RR	Before	6.50	222	296	2.8	186	102
	After	6.24	52	101	2.90	177	89

Textile wastewater sample of five industries from Gazipur, Bangladesh was investigated using the polyDADMAC (Table 3). Optimum flocculation was achieved at 0.2-1 ppm dosing of polyDADMAC. The pH of all samples was basic. COD removal efficiency (CRE) of NAZ Bangladesh Ltd., Tusuka Processing Ltd., Meghna Knit Composite Ltd., Zaintex Composite Ltd., and DIRD Composite Textiles Ltd. (unit-02) are 13.48%, 15.66%, 29.89%, 24.85% and 19.45% respectively. The decreased COD value in the treated wastewater signifies that the organic dyes were deposited as sludge with the effect of polyDADMAC coagulant. The polyDADMAC is found less effective in COD removal of textile wastewater than from the standard dye solution. This may be due to the pH of the wastewater samples. As all the wastewater samples were basic, there are high concentrations of negative ions in the wastewater sample. The dosage of polyDADMAC was not sufficient to neutralize excess negative ions to form flocs. Moreover, it might be due to molecular weight of the polyDADMAC as well. As gel permeation chromatography (GPC) of the polyDADMAC could not be obtained, we cannot comment on the influence of molecular weight of polyDADMAC on floc formation. TDS and TSS also decreased after treatment with polyDADMAC.

Table 3. Textile effluent status of before and after polyDADMAC treatment.

Company Name	Treatment Condition	pH	BOD_5 (mg/L)	COD (mg/L)	DO (mg/L)	TDS (mg/L)	TSS (mg/L)
NAZ Bangladesh Ltd.	Before	9.23	450	675	1.80	1680	235
	After	8.2	50	584	4.85	1592	132
Tusuka Processing Ltd.	Before	9.80	417	415	3.00	1287	297
	After	9.10	49	350	5.00	1195	120
Meghna Knit Composite Ltd.	Before	9.40	330	485	1.88	2153	390
	After	8.65	39	340	5.90	1021	110
Zaintex Composite Ltd. Gazipur	Before	11.42	207	696	2.12	2450	282
	After	9.88	72	523	4.62	1380	185
DIRD CompositeTextiles Ltd. (Unit-2), Gazipur	Before	9.39	117	293	1.46	2344	235
	After	9.03	66	236	4.78	1441	147

CONCLUSION

Microwave assisted synthesized polyDADMAC has shown some effectiveness in textile wastewater treatment. COD removal efficiency of actual textile wastewater is below 30% whereas the standard dye sample shows about 50-60% COD removal efficiency. This may be due to the basic pH of the wastewater. Better efficiency could be obtained if pH of the actual textile wastewater is kept around 7 before adding polyDADMAC.

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