

# Polyurethane green composites for the treatment of boron present in the oil produced water

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## Research

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# Abstract

Polyurethane (PU) based algae biocomposite is synthesized and tested for boron removal from oil produced water. The percentage of algae is varied in the biocomposite and its physical and chemical properties are evaluated. The surface morphology, crystalline structure, thermal stability is characterized using scanning electron microscope, fourier transform infrared spectroscopy and thermal gravimetric analysis. The density of synthesized PU/algae composites is in the range of 1.12 and 1.20 g/ml based on content of filler in the PU matrix. Weight losses of the tested specimens in various chemical solutions are less than 10%. The boron removal efficiency is in the range of 84–85%, depending upon the algae filler at pH 7.19.

## 1.0 Introduction

Oil industry worldwide produces large amounts of oil produced water (OPW). OPW accompanies with crude oil during the production process. OPW is highly saline with various inorganic and organic pollutants. The disposal of OPW is a big challenging task for oil producing companies. Treat and reuse of OPW is viable option other than injection to the oil wells in an enhanced oil recovery process (Feroz, et al., 2017). Boron is one of the major chemical contaminant in OPW (Ezerie, et al., 2012). The treated OPW for reuse should follow WHO standards of 0.5 mg/L (WHO, 2011). Treatment of boron in water and wastewater systems is a bit tedious (Bick and Oron, 2005). Various methods include reverse osmosis, adsorption, ion exchange, electro dialysis, electrocoagulation, and co-precipitation applied for the removal of boron from aqueous systems (Melnyk, et al., 2005, Turek, et al., 2007, Koseoglu, et al., 2010, Alper, et al., 2012, Jonna, et al., 2013, Ruiz, et al., 2013, Demey, et al., 2013). The combination of biomaterials with synthetic polymers is a good alternative to traditional products. This biocomposite will address the pertaining environmental and social issues in today's life (Murtuza, et al., 2010, Murtuza, et al., 2012). It is a great advantage that abundant available biomaterial such as algae can be utilized to produce valuable polyurethane polymer composite. Using algae as filler is having many advantages. Low cost, renewability, environmental friendly, non-toxic, high strength and low density (Tamara, et al., 2016, Ciecierska, et al., 2016). In the present research, an attempt is made to treat boron present in the oil produced water with synthesized polyurethane algae based biocomposite. The performance of adding the algae additives on PU properties is studied with different mass ratios. The characterization of the formed PU polymer with different algae composition is carried out to estimate the effects of amount of filler content on the density, chemical resistivity, crystalline structure and thermal stability.

## 2.0 Materials And Methods

### 2.1 Materials

Tolyene 2,4 Diisocyanates (TDI) of analytical grade (95%), Dibutyltin dilaurate (DLDBT), Methyl isobutyl ketone (MIBK) is purchased from Sigma- Aldrich, Germany. Castor oil (CO) is procured from local markets. Castor oil is only the natural oil polyol available in the market, which is produced directly from a

plant sources without chemical modifications. An alga is extracted from the sea rack, which is glued to the rock surface. The algae is dried and crushed into powder form. Before mixing algae with polymer, it was screened by sieve mesh size 300 micro to get uniform particle size. The filler density is estimated as 1.27 g/ml.

## 2.2 Synthesis of PU/Algae biocomposites

50 ml of methyl iso butyl ketone (MIBK) solvent is placed in the necked round bottom flask. Calculated amounts of tolylene 2,4 disocyanates (TDI), castor oil (CO) and 3 drops of catalyst dibutyltin dilaurate (DLDBT) are added to MIBK solvent as per standard procedure (Madhukar, et al., 2015). The flask is then kept on digital hot plate fitted with a condenser. The temperature is maintained between 60–70°C and stirred at 1200 RPM. The reaction between the aromatic TDI isocyanates, which is having two isocyanates groups (NCO) and a hydroxyl group (present in the castor oil) in the presence of catalyst DLDBT produce urethane groups as shown in the equation 1.



The algae powder is added to the PU solution after 30 minutes of mixing with different polymer-algae weight ratios (100/0, 97.5/2.5, 95/5, 92.5/7.5 and 90/10). PU/algae is stirred again for 1 hour. The resulting viscous solution poured into clean glass mold of dimension of 20×10×4 cm to get the uniform polymer film. The solution is cooled and dried slowly under ambient temperature overnight. The created PU sheet in the glass mold has been post cured in the electric oven at 60°C for 5 hours. The prepared biocomposite sheets are taken out and stored for characterization and experimentations.

## 2.3 Collection of OPW

Oil Produced water (OPW) is collected from (Oxy-Oman) site (Makizina) for this experimental purpose. Mukhaizna field is located in Oman's south central interior and it is producing very high viscosity oil. The initial boron and other multi component concentrations are estimated using plasma atomic emission spectrometry (ICP). The initial boron concentration in the produced water is obtained as 6.44 mg/l. The initial pH value of OPW sample is measured as 7.19.

## 2.4 PU/Algae Characterization

ASTM D792–08 method is used to determine the experimental density of the specimens. The weight of the specimen is taken in the air and in immersed water at room temperature to determine the specific gravity. Accordingly calculated the density of PU/Algae polymer specimens. The theoretical density is calculated for the composites by the weight additive principle as shown in equation 2 (Madhukar, et al., 2015).

$\rho = \omega_1\rho_1 + \omega_2\rho_2$  (2) Where  $\rho$  is the density of composite,  $\omega_1, \rho_1, \omega_2, \rho_2$  are the weight fraction, the density of the filler and neat polymer respectively.

The chemical resistance of PU/Algae polymer composites is studied in the various chemical reagents such as acids, basis, salts and organic solvents. Uniform surface area of PU/Algae composites is taken and immersed in the prepared chemical solutions for 7 days under laboratory environment. After 7 days, the specimens are removed and wiped with tissue papers and weighted. Then, the percentage weight changes are calculated. Also, surface to mass of the specimens are estimated. The morphological behavior, chemical composition and crystalline structure of the PU/algae composites is investigated by using scanning electron microscopy (SEM) technique with an operating voltage of 15 kV, magnification of 1000x and quality resolution of 10 microns. FTIR spectroscopy is used to analyze the physiochemical properties of synthesized PU/Algae composites as per standard procedure in the range of wave number 600 to 4000  $\text{cm}^{-1}$  (Marek, 1993).

A thermal property of polymer is investigated by using thermal gravimetric analysis (TGA) in order to determine the test conditions and the behavior of the polymer with increasing temperature. The sample is cut into a small piece and after that loaded into sample ceramics pan to complete thermal analysis. The nitrogen gas grade 5 is used as purge gas and it is supplied at a constant flow rate 100ml/min. The thermal analysis in TGA is started in the temperature range between 32 and 38°C and the final temperature considered for this analysis is 800°C. The heating rate is customized at 10°C/min. The thermograms are interpreted for all composites by using TA instrument explorer software universal V4.7A.

## 2.5 Boron adsorption characteristics

The treated oil produced water (OPW) is analyzed to examine the boron adsorption efficiency for different PU/algae composites. The adsorbent dosage is fixed as 1 gram in 50 ml of OPW for all PU compositions. The agitation is adjusted at 100 RPM to assist the contact between adsorbent and the untreated OPW for 72 hrs. The final boron concentration is obtained using plasma atomic emission spectrometry (ICP) and then the removal efficiencies are estimated.

## 3.0 Results And Discussion

### 3.1 Physical Properties

Three specimens are taken from each sample to determine the average density of PU/Algae compositions. The changes in density in a single polymer sheet are due to localized differences in crystalline structure, loss of plasticizer, absorption of methyl iso butyl ketone solvent and differences in algae filler compositions. The densities of neat polymer and algae filler estimated as 1.124 g/ml and 1.27 g/ml respectively. Both theoretical and experimental values for the PU/algae green composites is estimated and tabulated in Table 1. The densities estimated are in the range of 1.12 and 1.20 g/ml based

on the content of the filler in the PU matrix. The density increases with an increase of the filler in green composite due to the restriction of soft PU to pass through the tiny space between the rigid filler particles. The experimental results are slightly higher than theoretical results. This is due to the aggregation of filler at a higher amount of the filler content and maybe the filler not wetted completely in the PU matrix (Madhukar, et al., 2015). The surface area of the uniform mass of specimens decreases with an increase in the filler content. This may be due to the passage of the high density filler into the gaps of the PU matrix. Hence, the higher filler content polymer has less surface area compared to the analogous mass of less filler content polymer.

**Table1: Physical properties of PU/algae composite**

PU/algae compositions	Density (g/ml)		Void content (%)	Surface to mass of the specimens (cm <sup>2</sup> /g)
	Experimental	Theoretical		
100/0	1.122188	1.122188	0	31.25
97.5/2.5	1.126353	1.125883	0.0004	26.67
95/5	1.162581	1.129578	0.0284	24.09
92.5/7.5	1.206	1.133273	0.0603	21.86
90/10	1.208182	1.136969	0.0589	21.16

## 3.2 Chemical Resistivity

The chemical resistivity of synthesized PU/algae polymer composites is studied in the various chemical reagents. The chemical resistivity study helps to understand, the applicable uses of the PU/algae. It shows to what extent the algae powder can stay in touch with the PU specimen under various chemical environments. The weight losses for different PU/Algae specimens are obtained after 7 days are shown in Table 2. The percentage weight losses of the tested samples in the various chemical agents are within acceptable limit which is less than 10%. Furthermore, it is observed that PU/algae composites are dissolved rapidly in the acidic and basic solution than other chemical solutions. There is no significant change in surface color and thickness of the PU/algae specimens in the various tested chemical solutions.

**Table 2: Chemical resistivity of PU/algae composites**

Chemical Reagent	Weight Loss for PU/algae Composition				
	100/0	97.5/2.5	95/5	92.5/7.5	90/10
5% Sodium Hydroxide, NaOH	2.87	5.24	4.0	7.73	6.55
5% Sulfuric Acid, H <sub>2</sub> SO <sub>4</sub>	1.98	5.65	4.96	6.50	6.31
5% Ethanol, C <sub>2</sub> H <sub>6</sub> O	0.5	2.13	2.69	1.42	1.92
5% Methanol, CH <sub>3</sub> OH	1.08	2.47	0.65	1.05	1.87
5% Sodium Carbonate, Na <sub>2</sub> CO <sub>3</sub>	0.18	0.25	0.30	0.55	0.21

### 3.3 Surface Morphology

The SEM images of different PU/algae composites are shown in Figures 1(A)–1(E). SEM images indicate that algae powder have been distributed and integrated properly in the PU matrix. The 5% of filler weight in the PU matrix (Figure 1C) is distributed uniformly compared to the other filler composites. All the SEM images shown good adhesion of the filler into PU matrix. It is observed, the roughness and deformation of the polymers increased with an increase of the algae filler content. It may be due to the restriction of soft PU to pass through the tiny space between the rigid filler particles.

### 3.4 FTIR Studies

FTIR spectra of PU/algae composites are shown in Figure 2. Most of the synthesized biocomposite polymers shown the absence of the peak between 2270 and 2280 cm<sup>-1</sup> indicating that no free NCO groups (Tamara, et al., 2016). All the isocyanate groups have reacted during the polymerization process. Furthermore, NCO group peak areas are increased slightly with an increase of algae mass ratio. This indicates the reactivity of urethane NCO group decreases with an increase in the algae green composition. OH group peaks are not observed for all the developed polymer composites as shown in the Figure 2. Complete reaction of OH group with isocyanates groups. It is also observed absence of Urethane - C = O vibration in the range of 1720–1730 cm<sup>-1</sup> for the 7.5% algae content and appearance of C = C aromatic vibration in the all the synthesized PU/algae composites. Table 3 illustrates the expected range of the peaks of FT-IR spectra of PU/Algae composites and the observed peaks from the estimated curves.

**Table 3: FTIR spectroscopy peaks of PU/algae composites**

Group	Expected Peak (cm <sup>-1</sup> )	Observed Peak (cm <sup>-1</sup> )				
		0	2.5	5	7.5	10
NCO Vibration	2270-2280	None	None	None	None	None
C=O Vibration	1700-1750	1726	1725	1726	1701	1726
Urethane -C=O Vibration	1720-1730	1726	1725	1726	None	1726
C=C aromatic Vibration	1520-1600	1533	1533	1533	1528	1530
C-H stretching	2840-3000	2922	2923	2923	2922	2923
OH vibration	3530-3550	None	None	None	None	None

### 3.5 Thermogravimetric analysis

TGA is used to estimate the thermal stability of the PU/algae composites. The obtained thermograms are shown in Figure 3. The TGA thermograms indicated that PU matrix with different mass content of algae are stable up to 70–75°C. The PU/algae composite degradation can be described in three stages. First stage at temperature range of 75–251.80°C, the sample loses about 5.29% of its initial weight due to the gradual evaporation of the methyl iso butyl ketone solvent and the slight degradation of the soft segment in the PU/algae composite. Second stage at temperature range of 251.80– 520°C, the sample losses about 88.46% of its weight attributed to thermal degradation of the hard segment and partially degradation of the algae component. Finally, the third stage starting at temperature 520°C up to upper limit temperature considered for this study (800°C), the sample loses about 2.14% of total weight due to decomposition of the algae composite and degradation of the remains hard segment and other associated compartments. More algae content has less weight loss, which indicates that algae can act as good filler for thermal degradation stability of PU polymer.

The relative thermal stability of the PU matrix with different algae content is estimated by comparing the decomposition temperatures at different weight loss percentages as shown in Table 4. The T0 is expressing the temperature of onset decomposing, whereas T10, T20, T50 and T70 expressing the decomposition temperature at 10, 20, 50, 70 weight loss percentage. The temperature of degradation of PU/algae composites is increased with an increase of algae content at different weight loss percentages. This lead to conclude that filler content is improving the relative thermal stability of the PU polymer. It can be act as a thermal insulator due the ability to block the volatile component during the thermal degradation analysis process.

Table 4: Effect of algae filler on the thermal stability of the PU matrix

Algae content in PU matrix	Sample weight (mg)	Temperature at different weight losses				
		T <sub>0</sub>	T <sub>10</sub>	T <sub>20</sub>	T <sub>50</sub>	T <sub>70</sub>
0	24.775	70	278	298	382	438
2.5	24.593	71	278	297	378	437
5	27.81	73	278	299	383	440
7.5	23.785	74	280	300	386	442
10	23.474	75	280	301	386	443

### 3.6 Boron adsorption studies

The boron removal from OPW is estimated for different PU/algae composites after 72 hours of contact time as shown in Table 5. The removal efficiency is in the range of 84 to 85%. The maximum boron removal efficiency is observed in case of neat PU polymer as adsorbent due to absence of filler and availability of space between PU matrix molecules. However, there is not much difference between the different PU/algae composites for boron removal efficiency. Figure 4 represents the boron presence in OPW after treating with various PU/algae matrix.

**Table 5: Boron adsorption efficiency of the PU/algae composites**

PU/Algae composition %	Contact time (hr)	Initial boron concentration (mg/l)	Final boron concentration (mg/l)	mg B removal/ g adsorbent	Removal efficiency (%)
100/0	72	6.44	0.958	5.482	85
97.5/2.5	72	6.44	0.987	5.453	84
95/5	72	6.44	0.989	5.451	84
92.5/7.5	72	6.44	0.982	5.458	84
90/10	72	6.44	1.02	5.42	84

### 4.0 Conclusions

This study investigated the performance of algae based PU polymer composites for the treatment of boron presence in oil produced water (OPW). PU/algae composites synthesized by varying the content of filler algae and their physical and chemical properties are estimated. The density of PU/algae composites is in the range of 1.12 and 1.20 g/ml based on content of filler. The density increases with an increase in algae content. The surface area decreased with an increase in the filler content of the uniform mass of PU/algae composites. Weight loss of the tested specimens in various chemical solutions are less than 10%, indicated stable chemical resistance by PU/algae biocomposites. SEM images showed the

proper distribution and integration of algae filler in PU matrix. The roughness and difficulty for deformation increases with filler content. FTIR spectroscopy indicates the absence of NCO peaks which indicates there is no free NCO group in the formed polymers. Thermogravimetric analysis showed with increases in filler content, the thermal stability increased. The boron removal efficiency is found to be in the range of 84% and 85% at pH 7.19.

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## Declarations

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Authors contribution: Mr. Mohammed Al Sawwafi carried out experimental work, Dr. Murtuza Ali Syed contributed in characterization and analysis. Dr. Shaik Feroz contributed in interpretation of data.

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## Figures

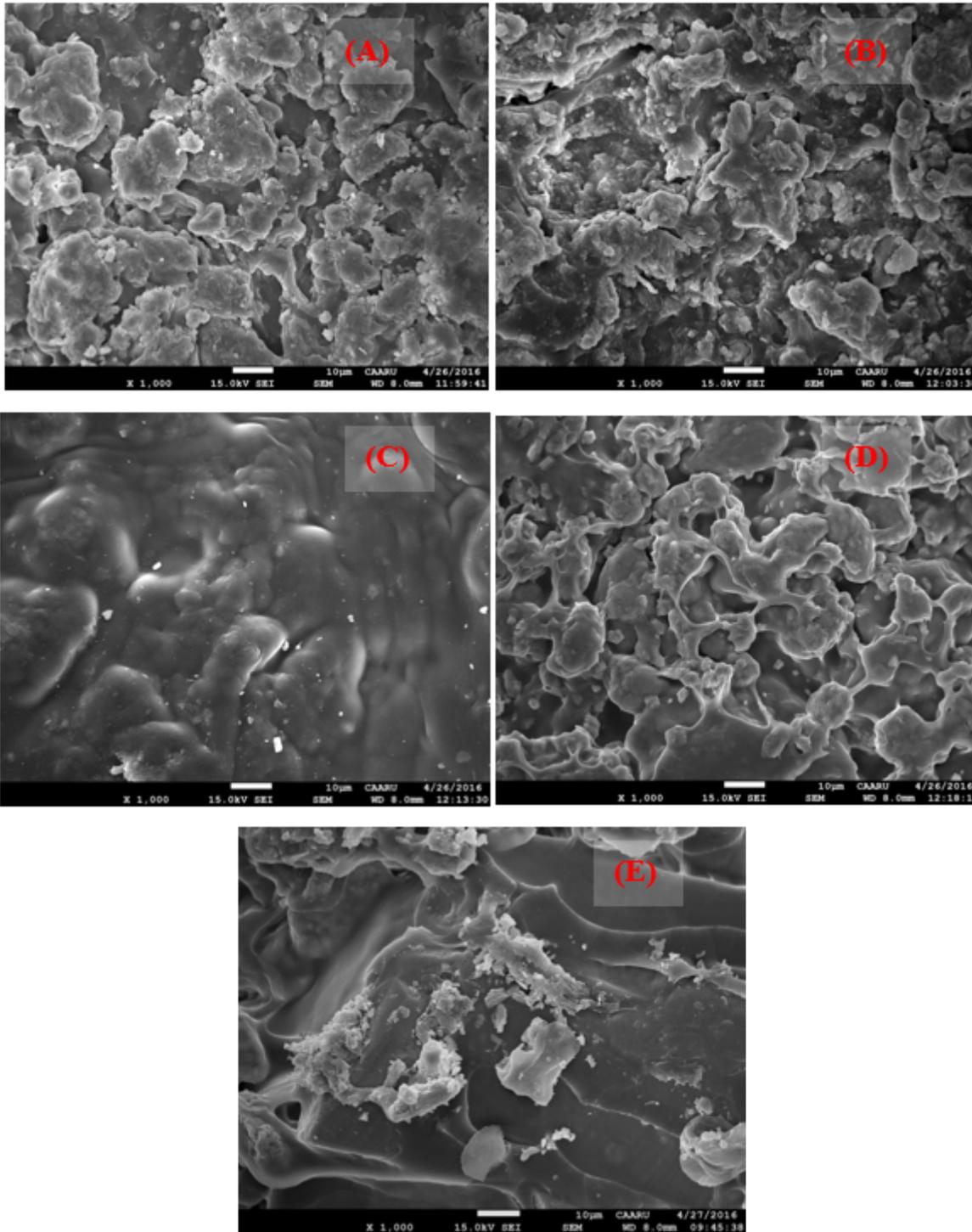


Figure 1

SEM images of PU green composites with (A) 0%, (B) 2.5%, (C) 5%, (D) 7.5% and (E) 10% of algae filler

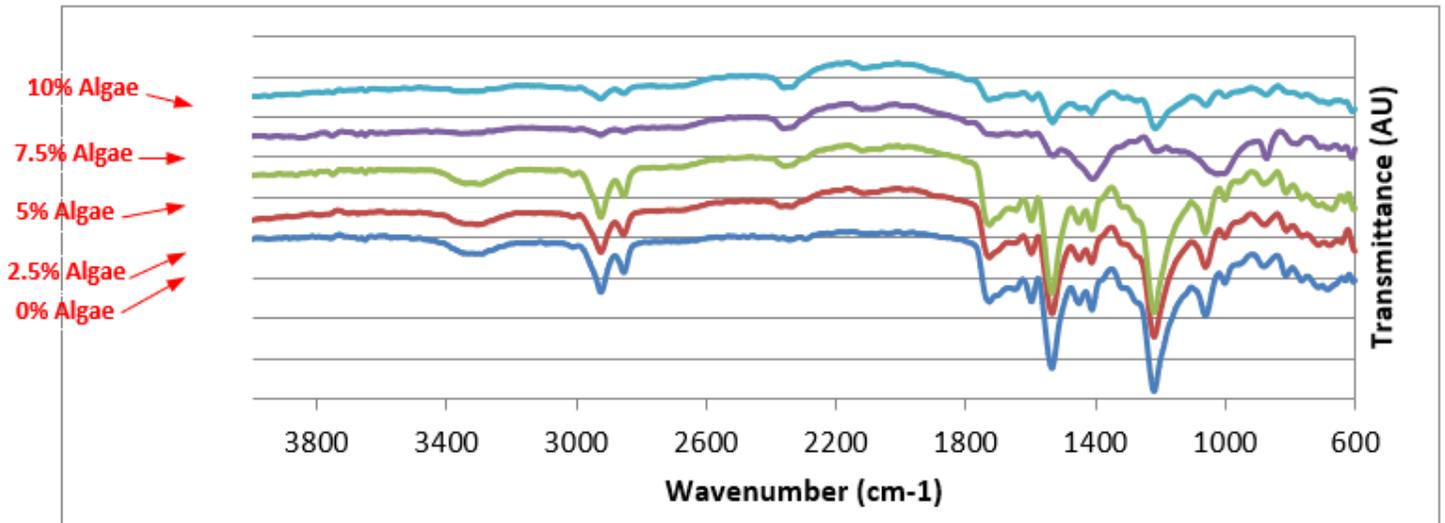


Figure 2

FTIR Spectra of PU/algae Composites

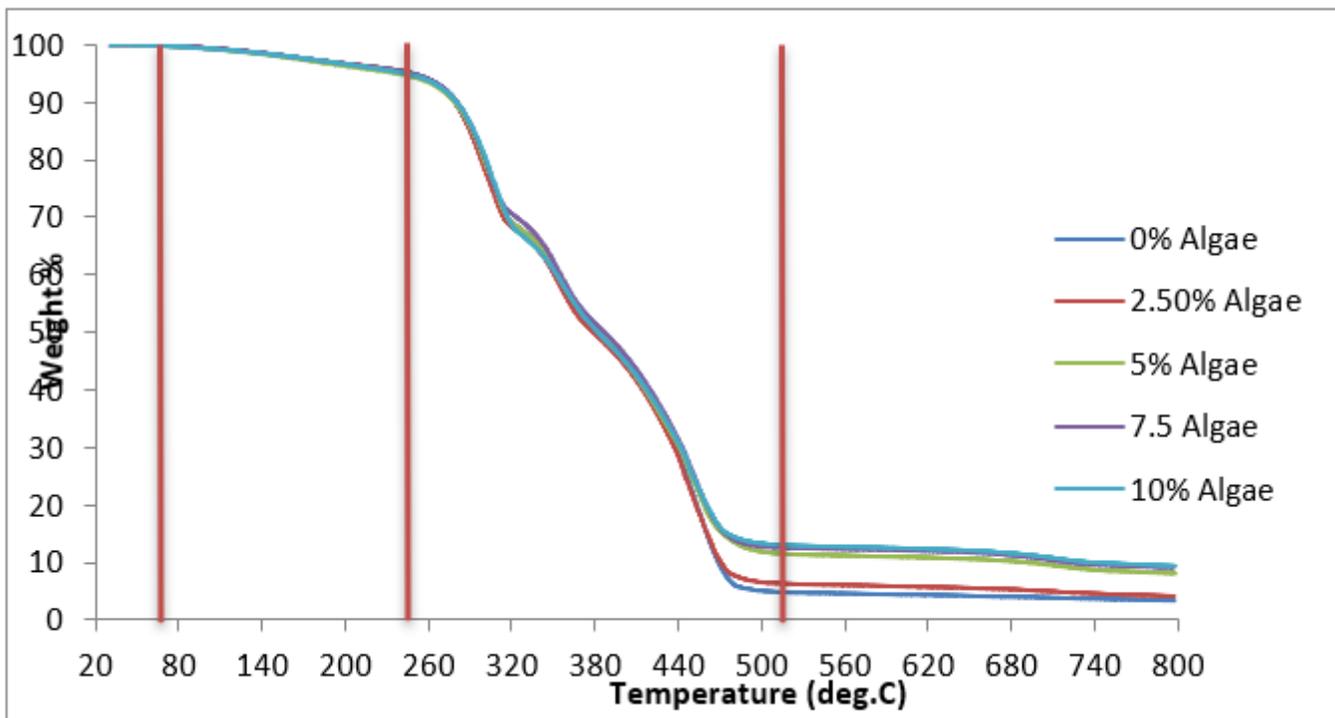


Figure 3

Thermograms of PU/algae composites

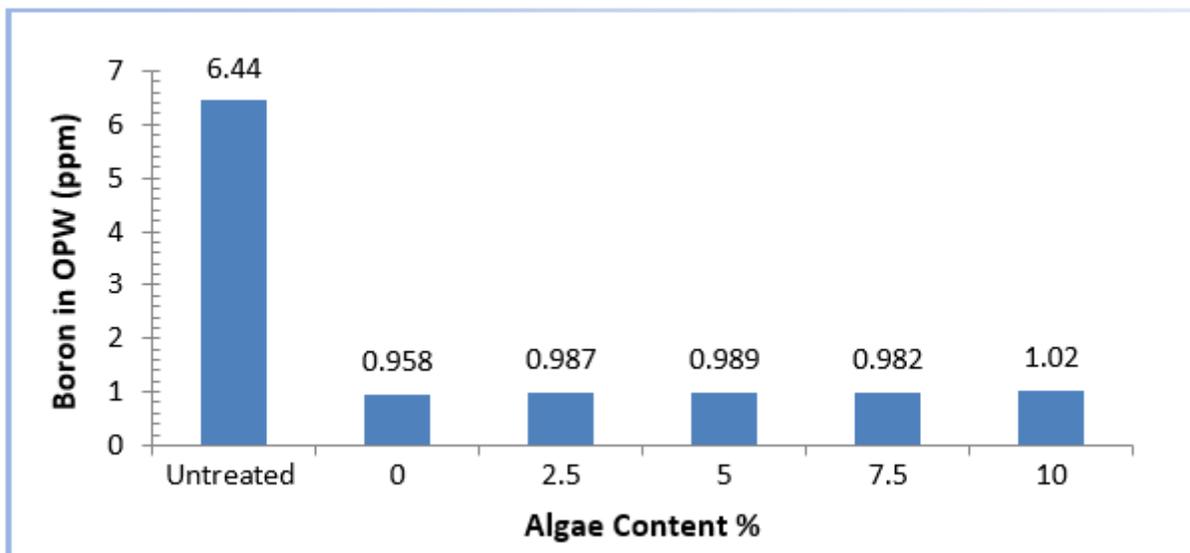


Figure 4

Boron content in OPW after adsorption on PU/algae composites