Chemical Oxygen Demand and Color Removal from Oil Refinery Wastewater using Chitosan Bio-adsorbent

Gugulethu Ngcobo[1], Siphesihle Mangena Khumalo[2], Emmanuel Kweinor Tetteh[3], Babatunde Femi Bakare[4], and Sudesh Rathilal[5]

Abstract— The discharge of untreated industrial wastewater with high organic pollutants poses a toxic health effect to humans and aquatic life due to the inability of conventional wastewater treatment plants to eradicate organic contaminants. Therefore, the current study focuses on the application of chitosan derived from food waste i.e., mussels and oyster shells as a bio-adsorbent for chemical oxygen demand (COD) and color removal from wastewater emanating from a South African oil refinery. Batch adsorption studies were conducted by investigating the effect of pH, adsorbent dose as well and contact time on the percentage removal of COD and color from waste oil refinery wastewater. At greatest conditions of 15g chitosan/L and contact time of 60 minutes, COD removal efficiencies of 83% (mussels) and 88% (oysters) were recorded. On the other hand, color removal efficiencies of 71% and 87% were achieved for mussels- and oysters-based chitosan, respectively. The high COD and color removal efficiencies by chitosan derived from oysters are ascribed to its high degree of deacetylation of 80,46% compared to the 76,92% recorded for mussels. The findings of the present study suggest that oyster-based chitosan can effectively address the issue of high COD and color from wastewater emanating from oil refineries as an environmentally green technology.

Keywords— chitosan, mussels, oysters, chemical oxygen demand

I. INTRODUCTION

Seafood waste contributes at least 30% of the total amount of food waste globally [1]. In South Africa a person consumes about 12kg of seafood per year on average [2]. Mussels and oyster shells are among the most common types of crustacean waste in municipal landfills. The rapid demand for seafood particularly in South Africa is ascribed to dietary changes which contribute significantly to the production of crustacean waste such as mussels and oyster shells. On the other hand, there has been a swift growth of industries like petrochemical industries, food processing, textile, steel, and leather manufacturing industries, etc. [3]. It is worth noting that industrial growth contributes significantly to the global economy, and industrial effluent characterized by toxic pollutants poses a serious threat to the environment. These harmful pollutants, particularly in wastewater streams, are available in high concentrations and trace amounts, requiring adequate removal from effluent streams before discharge into communal water bodies. As such, this study focuses on the removal of chemical oxygen demand (COD) and color from wastewater emanating from an oil refinery. Wastewater from oil refineries is characterized by high concentrations of COD and color intensity, indicating the presence of organic and inorganic pollutants. High concentrations of COD in water bodies result in the reduction of dissolved oxygen in water thus killing aquatic life and promoting eutrophication in water bodies. On the other hand, high color intensity hinders any photolysis process in water bodies.

Statistically, the world consists of 30 billion liters of oily wastewater [4] and this volume keeps on increasing with the increasing number of refineries due to oil demand. Treatment of oily wastewater is becoming an urgent need [5]. Hitherto different types of coagulation techniques have been assessed to mitigate this phenomenon, however, due to the complex composition of oil/water emulsion, the treatment becomes difficult which leads to other techniques failing, which poses the inability of wastewater reuse and high cost in the treatment of oil contaminated wastewater [6].

Agricultural and natural adsorbents like bamboo dust [7], barley straw[8], and sugar cane bagasse [9] have been used as a great option in wastewater treatment; so far, they have shown promising results and have a high absorption ability. Given their biodegradability and high molecular weight, these natural flocculants are promising to be substituted for conventional ones [10].However, according to [11], these materials adsorb water along with oil and have minimal oil loading capacity. Some of the biosorbents derived from the aforementioned

Gugulethu Ngcobo[1] is with the Green Engineering Research Group, Department of Chemical Engineering, Durban University of Technology, Durban, South Africa

Siphesihle Mangena Khumalo[2] is with the Green Engineering Research Group, Department of Chemical Engineering, Durban University of Technology, Durban, South Africa

Emmanuel Kwenior Tetteh[3] is with the Green Engineering Research Group, Department of Chemical Engineering, Durban University of Technology, Durban, South Africa

Babatunde Femi Bakare[3] is with the Department of Chemical Engineering, Mangosuthu University of Technology, Durban, South Africa

Sudesh Rathilal[4] is with the Green Engineering Research Group, Department of Chemical Engineering, Durban University of Technology, Durban, South Africa

agricultural wastes have the disadvantage of being pH-sensitive and poor performance in removing minute particles from aqueous solution [12].

Chitosan is a useful biosorbent component extracted from chitin, a substance found in crustacean shells [13]. Its application as a biosorbent in water treatment has attracted the attention of many researchers due to its perceptible benefits in mitigating the environmental burden. Chitosan is a polymer that is fractionally deacetylated. It is obtained from chitin, a polysaccharide of N-glucoside found in marine cell walls [14]. Therefore, chitosan is a biopolymer extracted from chitin employing alkaline deacetylation. It is characterized by an acetamide group in the structure, shown in Fig. 1 [15], [16].
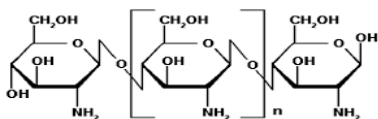

Fig. 1: chitosan structure adapted from [17]

Chitosan's positive charge and amino group properties make it an excellent choice for wastewater treatment. Chitosan helps to improve coagulation, making it an essential component in wastewater [18].

Several methods are employed to determine and confirm chitosan, however, the most essential method of confirmation is through the degree of deacetylation (DD) [19]. This parameter which indicates the molar percentage of glucosamine indicates whether the biopolymer is chitin or chitosan and its quality[19], [20].

The level of pollution in wastewater is reflected by the intensity of its color [21] If the concentration of COD is high, it can react with chlorine in the final water treatment process to produce trihalomethane (THM), which is a toxic compound that can have negative health effects, such as cancer [22]. Various techniques, such as nanofiltration [23] and electrocoagulation [24], have been evaluated for removing COD and color. However, this study focuses on the use of the bio-adsorbent chitosan to eliminate COD and color from oil refinery wastewater.

II. MATERIALS AND METHODS

A. Materials

The waste shells utilized in the present study were obtained from a seafood restaurant located in Durban, South Africa. Analytical grade NaOH and HCl were procured from Merck Chemicals in South Africa.

B. Sample Collection and Preparation

Raw wastewater samples were collected from a South African oil refinery at the effluent stream of the plant. Samples were collected and filtered on-site to remove debris. The filtered samples were collected in 1L umber sampling bottles to avoid any photolysis and transported in a cooler box full of ice to maintain the sample's biological conditions. Fresh samples were characterized for the parameters as presented in Table I prior to the commencement of experimental runs.

TABLE I
OIL REFINERY WASTEWATER SAMPLE COMPOSITION

Parameter	Mean±SD
pH	7.05±1.8
COD (mg/L)	2029±18.6
Turbidity (NTU)	80.5±3.5
Color (mg/L)	1955±48.1
Phenol Content (ppm)	1948±35.1

C. Adsorbent preparation

Waste Shells of oysters and mussels were acquired from a nearby seafood restaurant in Durban South Africa. The shells were thoroughly cleaned using deionized water and dried before being crushed. They were crushed into a mixture of flakes and powder.

Chitosan production was done by soaking 500g of shell powder in a 1 L solution of 5% NaOH under controlled temperature conditions of 100°C for 3 hours. This was done to remove any protein compounds found in both oyster and mussel shells. Thereafter, the deproteinized powder was rinsed using deionized water until a pH of 7 was reached prior to drying at 100°C for 2 hours. The dried deproteinised powder was soaked in a 1 L solution of 5% HCL at a temperature of 100°C for 1 hour to produce chitin, which was then rinsed with deionized water to achieve a pH of 7. The chitin wet powder was then dried at a temperature of 100°C for 2 hours. Dried chitin powder was then bleached by soaking it in a solution of 0,135 NaOCl for 24 hours and rinsed with deionized water to a neutral pH. The bleached chitin underwent deacetylation to produce chitosan (see Fig.2) by being heated in a 50% NaOH solution for 2 hours. Thereafter, the produced chitosan by deacetylation was rinsed with deionized water and dried at 65°C for 4 hours.
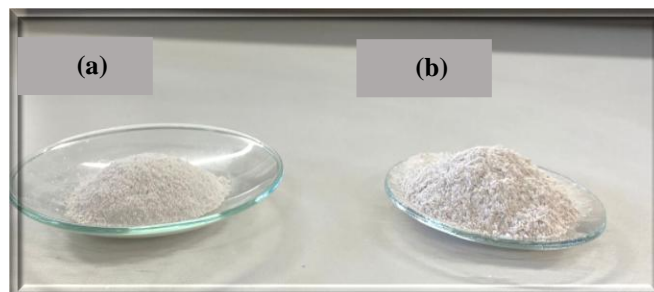

Fig.2 chitosan powder from mussel shells (a) and oyster shells (b)

The degree of deacetylation and molar mass of the synthesized chitosan was determined using the Linear

Potentiometric Titration method, as outlined[25]. The degree of deacetylation (DD) was computed using (1).

$$DD\ [\%] = \frac{\alpha}{\frac{w-161\times\alpha}{204}+\alpha} \times 100 \qquad (1)$$

Where α is the amount of N-acetyl glucosamine
$\frac{Na.Va-Nb.Vb}{1000}$
W is chitosan sample mass in g

.D. *Jar Test System*

Adsorption studies were conducted using a standard laboratory jar test method to investigate the effect of adsorbent dosage and contact time in the removal of COD and color from wastewater emanating from an oil refinery.

Lovibond ET 750 consisting of six 1000 mL graduated beakers each beaker with a paddle for starring was utilised. The experimental study was conducted for three systems each with an adsorbent dose of 3g/L, 9g/L, and 15g/L. 500 mL of raw wastewater was added to a beaker with the corresponding adsorbent dosage, the agitating speed was maintained constant at 250 rpm. For each system, sample analyses were conducted over a time interval of 15 minutes. Prior to analysis, samples were allowed to settle for a predetermined time of 30 minutes, thereafter, the clear supernatant was syphoned using a pipette. The syphoned supernatant was immediately analyzed for COD and color using the HACH DR900 spectrophotometer. Experimental runs for both chitosan derived from oyster shells and mussel shells were conducted at a pH of 7. pH adjustments were conducted using 1.0M HCl and 1.0M NaOH.

The systems' removal efficiency for COD and color, was calculated using equation (2):

$$Y(\%) = \frac{C_{initial} - C_{final}}{C_{final}} \qquad (2)$$

where Y (%) is the removal efficiency in terms of COD and/or color; $C_{initial}$ and C_{final} are the initial and final concentrations of the targeted contaminants, respectively.

III, RESULTS AND DISCUSSION

A. *Chitosan Characterization*

Vibration results measured in cm^{-1} for the Fourier-transform infrared (FTIR) spectroscopy are shown in Fig. 3 and Fig. 4. The spectrum for oyster-based chitosan in Fig. 4, the band 3655 cm^{-1} suggests the presence of an O-H stretching bond, 2924 cm^{-1} attributes the N-H stretching bond, vibration 1577 cm^{-1} confirms N-H bending bond, there is also an indication of a O=C=O at vibrations 2349 cm^{-1} bend which could be a possible nanochitosan. This spectroscopy is congruent with the work reported by [26], thus suggesting chitosan properties for the synthesized adsorbent.

The spectrum for mussel chitosan in Fig. 4 also follows the above trend, however, the vibrations for the second amine

group is not evident in the structure. These findings indicate that the chitin component was not completely removed.
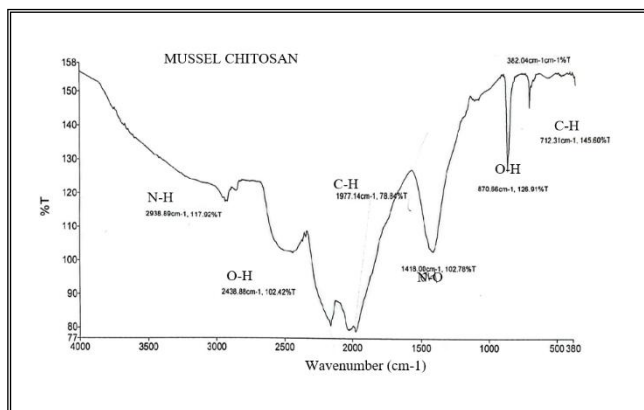

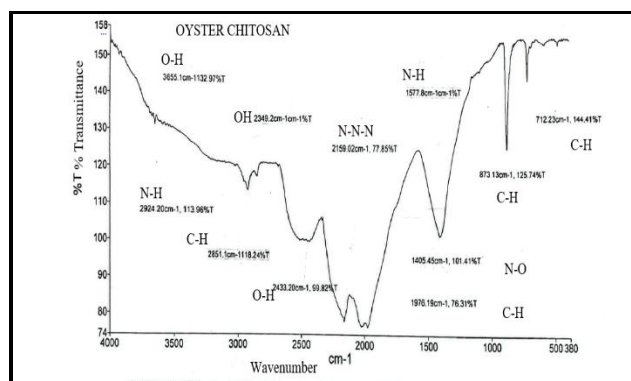Fig.3 FT-IR spectrum for mussel shell-based-chitosan

Fig.4 FT-IR spectrum for oyster shell-based chitosan

Scanning Electron Microscopy (SEM) in conjunction with Energy Dispersive X-ray (EDX) was used to characterize the morphology and element distribution of chitosan. Carbon was employed to cover all samples throughout this examination. Upon analysis, pictures were acquired at a high voltage of 20Kv using a TESCAN Vega TC equipment linked with an X-ray detector. The EDX was retained at 5Kv and was used to determine the morphology of the components found in chitosan. The results in Fig. 5 and Fig. 6 suggest a high calcium content, which is beneficial considering calcium-based adsorbents are effective [27, 28]. SEM confirmed the spherical morphology and homogenous size distribution.
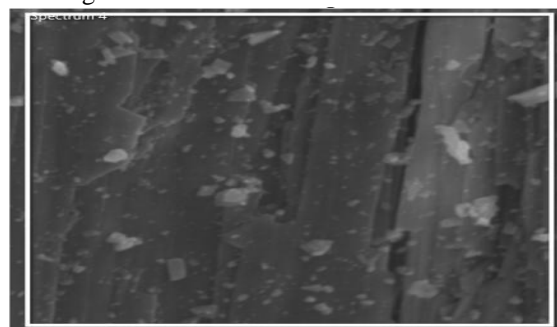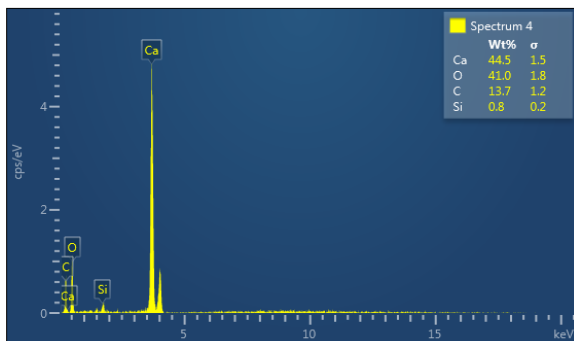

Fig.5 SEM analysis image for oyster chitosan

Fig. 6 EDX analysis for oyster chitosan

B. COD and Color Removal Using Chitosan

Fig.7 and Fig.8 depict the findings of the present study on COD and color removal from wastewater emanating from a South African oil refinery. From the findings presented in Fig.5, it can be observed that oyster-based chitosan demonstrated higher COD removal efficiencies of up to 88% when compared to mussel-based chitosan with a removal efficiency of 83 %. The observed results can be ascribed to the high degree of deacetylation for oyster-based chitosan of 80.46 % compared to 72.96 % for mussel-based chitosan. Similarly, the same trend was observed for color removal with oyster-based chitosan recording a removal efficiency of 87% and mussel-based chitosan recording a removal efficiency of 71%. As such, the high degree of deacetylation suggests that oyster-based chitosan structure had a higher composition of functional groups necessary for COD and color removal from aqueous environments when compared to mussel-based chitosan.
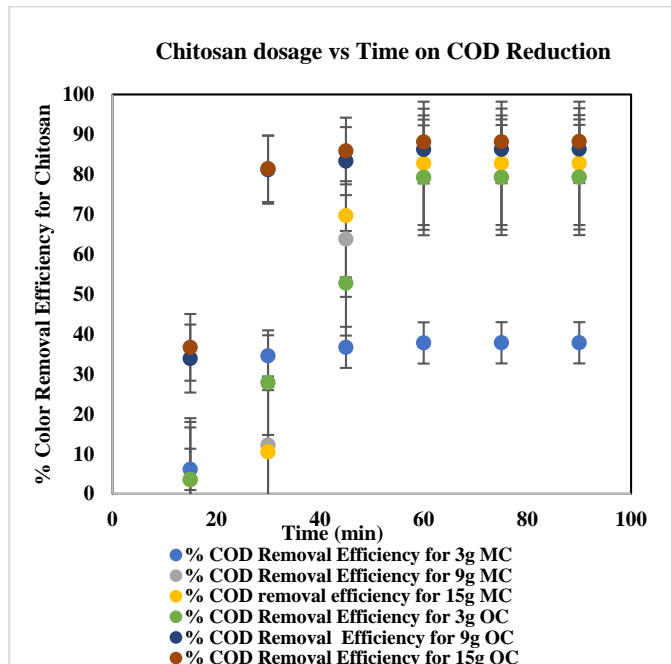

Fig. 7 Chitosan Color removal efficiency

Fig. 8 Chitosan COD removal efficiency

C. Effect of Biosorbent Dose

By adjusting the chitosan dosages, absorption effectiveness was tested It was observed that the optimal dosage for oyster-based chitosan was achieved at 9g, as there was only a slight difference in removal efficiency between 9g and 15g (see Fig 5). On the other hand, mussel-based chitosan showed that higher dosages resulted in better removal efficiency, with the highest color removal efficiency found at a 15g dosage (Fig 6). Optimum conditions were achieved, and the color removal rates for mussel and oyster chitosan were 71.2% and 87.49%, respectively. The COD removal efficiency for mussel and oyster chitosan was 83% and 88.1%, respectively.

D. Effect of Contact Time

The effect of contact time in COD and color removal is important. During the experiment, the duration of operation was recorded while utilizing chitosan as the biosorbent. The efficiency of COD and color removal was measured at various contact times when treating oily wastewater samples with chitosan. Fig. 5 and Fig 6 illustrate that even in small dosages the removal efficiency increases when contact time is increasing. A noticeable change was observed between 45 and 60 minutes of contact time.

E. The Overall Impact of Prepared Chitosan in Removing COD and Color.

This work has shown that the eco-friendly removal of COD and color from concentrated oily wastewater using biopolymer chitosan is a feasible and affordable solution. Pre-treatment is advised since it can reduce the quantity of biosorbent required for treatment.

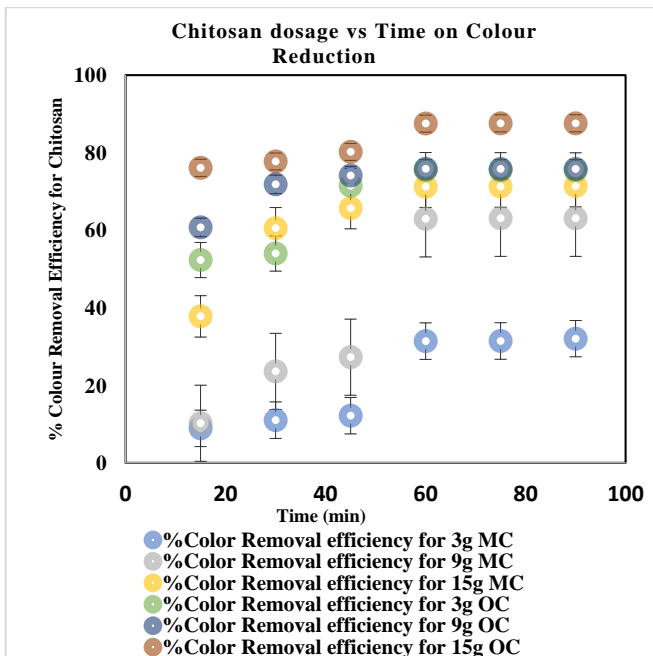The COD and color removal effectiveness patterns are

similar to those of previous researchers, ,[29] , but this study's COD and color removal using chitosan outperforms that of other researchers [30]. Results show that the level of prepared chitosan is adequate.

CONFLICTS OF INTEREST

The authors have declared that they have no conflicts of interest. Additionally, they have included references to support their work.

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