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PHYSICO-CHEMICAL ANALYSIS OF TEXTILE EFFLUENT COLLECTED FROM TIRUPPUR BEFORE AND AFTER TREATMENT WITH CRAB (*PORTUNUS SANGUINOLENTUS*) SHELL CHITOSAN

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ABSTRACT

Textile industries are one of the main sources of wastewater containing high amounts of colour, pH, BOD, COD, DO, TDS, TSS, alkalinity, chloride, phosphate, hardness, chemicals and heavy metals. They contaminate the water bodies and its ecosystem. In the present investigation, textile wastewater was collected from the discharge tank of a Tiruppur textile industry to investigate eleven physico-chemical parameters such as colour, total solids, TDS BOD, COD, Total alkalinity, Total hardness, chlorides, sodium, sulphates and iron. Chitosan extracted from crab shell is selected as an absorbent to reduce most of the aforesaid parameters present from the textile industrial waste water. The percentage removal of colour, total solids, TDS BOD, COD, total alkalinity, total hardness, chlorides, sodium, sulphates and iron were 32.61 mg/l, 90.97 mg/l, 91.81 mg/l, 61.72mg/l, 55.66 mg/l, 91.57 mg/l, 45.90 mg/l, 96.76 mg/l, 66.73 mg/l, 80.77 mg/l and 94.79 mg/l respectively.

KEY WORDS: Textile industry, Alkalinity, Chloride, Physico-chemical, Chitosan, Effluent, Colour.

INTRODUCTION

In India, most of the industries are located along the river banks because of easy availability of water and disposal of wastes. The textile industry releases large amount of liquid wastes that contain organic and inorganic compounds. During the process of rinsing, various chemicals including salts, metals, surfactants, sulphides, formaldehyde are used. Low pH, high electrical conductivity, high concentration of ions of sulphate and iron, toxic heavy metals, low Dissolved Oxygen(DO) and high Biochemical Oxygen Demand (BOD) in the effluent are some of the parameters that characterize the degradation of water quality. High levels of Chemical Oxygen Demand (COD) and (BOD) and high temperatures which lower the rate of dissolution of oxygen in water affects the aquatic habitats. Uptake of textile effluent through food chain in aquatic organisms can cause various physiological effects like hypertension, sporadic fever, renal damage, cramps, tumors, cancers and allergies in humans and acts as growth inhibitors in different trophic levels in aquatic ecosystem (Bakshiand Sharma, 2003).

The higher level of pH indicates alkalinity conditions of soil which affects the soil micro flora and permeability (Robinson *et al*., 2002). Excessive turbidity in water provides food and shelter for pathogens. High Total Suspended Solids (TSS) in water body can often mean higher concentration of bacteria, nutrients, pesticides and metals in water. Water withhigh Total Dissolved Solids (TDS) is not recommended for drinking and irrigation purposes as they may cause salinity problems. High levels of COD in water can cause threats to human health as well as a decrease in the amount of dissolved oxygen available for aquatic organisms. Higher level of BOD indicates the pollution strength of waters.

Chitosan can be recommended as a good adsorbent which is naturally found in the exoskeleton of crustaceans, insects and some fungi. Chitin is the second most abundant naturally occurring biopolymer, which is largest source of exoskeletons of arthropods, especially crabs, insects and also the cell walls of fungi. The dry weight of chitin is highest in crustaceans. Crab shell is made up of three basic components such as chitin (15-40%), protein (20-40%) and a calcium and magnesium carbonate salt (20-50%) (Antonino *et al.*, 2017) Chitin is the fairly completely acetylated polysaccharide in nature, after cellulose. Chitosan is relatively a nontoxic, cheap and biodegradable polymer when compared with other polymers. It can be used as a coagulant, bactericide, pollutant reducing agent for removal of organics, suspended solids, turbidity, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) (Chen *et al*., 2005; Chung, 2006; Feng *et al*., 2000; Megeti, 2000).

The present study aims to demonstrate the application of chitosan as a bio-adsorbent for reduction of colour, total solids, total dissolved solids, biological oxygen demand, chemical oxygen demand, total alkalinity, total hardness, chlorides, sodium, sulphates and iron from the textile effluent.

MATERIALS AND METHODS

Sampling

The textile effluent was collected from a textile industry in Tiruppur. A sterile plastic was used to collect the textile wastewater. The effluent was transported to the laboratory and refrigerated until further analysis in accordance with the standard methods (APHA, 2017).

Bio-adsorption treatment of textile effluent

For bio-adsorption experiment, 10g of crab shell chitosan was added to 2 liters of the textile effluent in a 2000 ml conical flask for 30 days. Aftertreatment, the following parameters were assessed.

Colour (APHA, 2017)

The colour is measured by Multi-wavelength method.

Total Solids (TS) (Indian Standards, 2019) **and Total Dissolved Solids** (IS, 2018)

Total Solids and Total Dissolved Solidswere calculated by evaporating the sample in a weighed dish. Heat the clean evaporating dish to 180°C for 1 hour. Cool, desiccate, weigh and store in desiccator until ready for use. 250 ml of textile wastewater was added to the sample dish. Pipette this volume to a weighed evaporating dish placed on a steam-bath. Evaporation was performed in a drying oven. The temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample. After complete evaporation of water from the residue, transfer the dish to an oven at 103-105 °C, or 179-181 °C and dry to constant mass, till the difference in the successive weighing is less than 0.5 mg. Weigh the dish as soon as it has cooled. Total Solids and the Total Dissolved Solids were calculated by following formulae,

Total residue, mg/l = $\frac{1000M}{V}$

Where,
M = mass in mg of total residue, and
V = volume in ml of the sample.

Chemical Oxygen Demand (COD) (APHA, 2017)

A suitable volume of textile effluent was taken in a tube or ampule. One or more standards were prepared, digested, and cooled. The contents of reaction vessels were mixed to combine condensed water and dislodge insoluble matter. Absorption of each sample blank and standard was measured at selected wavelength (420 nm or 600 nm). Blank COD was subtracted from sample. At 420 nm, reagent water was used as a reference solution. The absorption measurement of an undigested blank containing dichromate, with reagent water replacing sample, will give initial dichromate absorption. The difference between absorbance of a given digested sample and the digested blank is a measure of the sample COD.

Biochemical Oxygen Demand (BOD) (IS,2020)

The distilled water was aerated in a container by bubbling compressed air for 8 to 12 hours and let to stabilize for 4 hours. 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride were added for each litre of dilution water. 2 to 5 ml of textile effluent was added per litre of dilution water for seeding purpose. The sample was neutralized to pH around 7.0 using alkali or acid and expected BOD was determined. Initial DO in two bottles was determined and remaining four bottles were incubated at 27°C ± l°C for 3 days. After 3 day's incubation at 27°C ± 1 °C, final DO was determined in incubated bottles

Chlorides (IS, 2020)

Chlorides were analyzed by Argentometric Method. Use 100 ml sample or a suitable portion diluted to 100 ml. Titrate the samples after adjusting the pH range to 7 -10 by adding sulphuric acid or sodium hydroxide. Add 1.0 ml of potassium chromate indicator solution. Titrate with standard silver nitrate solution to a pinkish yellow end point. Standardize silver nitrate solution and establish reagent blank value by titration method.

Total Alkalinity (IS, 2020)

20 ml of sample was pipetted into 100-ml beaker. Add 2 to 3 drops of phenolphthalein Indicator and titrate with standard sulphuric acid solution till pink colour just disappears which shows equivalence of pH 8.3. The volume of standard sulphuric acid solution used was recorded. 2 to 3 drops of mixed indicator were added to the solution in which the phenolphthalein alkalinity has been determined. Titrate with the standard acid to light pink colour (equivalence of pH 3.7). The volume of standard acid used was recorded after alkalinity.

Total Hardness (IS, 2020)

An aliquot of the sample was digested with 3 ml of concentrated nitric acid in a beaker on a hot plate and evaporate to near dryness cautiously making sure that the sample does not boil. Digestion was repeated with nitric acid till the digestate is light in colour. Evaporate to near dryness and cool the beaker. A small quantity of 1:1 hydrochloric acid (5 ml) was added and warmed on a hotplate or steam-bath to dissolve the residue. Then it is cooled, adjusted to a suitable volume and an aliquot of this digested sample was taken. An aliquot of water sample, maximum 50 ml, was pipetted in a porcelain dish or 150-ml beaker and the volume was adjusted to approximately 50 ml. 1 ml hydroxylamine hydrochloride ($NH_2OH.HCl$), was added to the solution. 1 to 2 ml of buffer solution was added so as to achieve pH of 10.0 to 10.1. 2 ml Eriochrome black T indicator solution was added, titrate with standard EDTA solution stirring rapidly in the beginning and slowly towards the end till end point is reached when all the traces of red and purple colour disappear and the solution is clear sky blue in colour.

Sulphates (IS, 2020)

Suphates in the sample was estimated by turbidity method. Take 20 ml of clear aliquot of the water sample or suitable amount diluted to 20 ml in l00 ml conical flask. Add 1.0 ml hydrochloric acid solution and 1.0 ml conditioning reagent and mix well for 30 seconds. Read the absorbance on spectrophotometer.

Sodium (IS, 2019).

50 ml textile effluentis diluted and pipetted into pyrex beaker and evaporated to dryness on a steam or hot water bath. The residue is cooled and 1.0 ml distilled water was added. Treat with zinc uranyl acetate reagent. Mix, cover the beaker and let it stand for or 1 hour. Collect the precipitate under suction in a weighed medium porosity sintered glass crucible. Drain the filter as dry as possible under suction. Wash the beaker, crucible and precipitate five to eight times with 2 ml portions of zinc uranyl acetate reagent. Conclude the washing with three small portions of diethyl ether.

Continue suction for a few minutes until the diethyl ether is dry. Transfer the crucible to the balance and weigh after 10 to 15 minutes and again 10 minutes later to check on the constancy of the mass. Return the crucible to the suction apparatus and dissolve the sodium zinc uranyl acetate by passing 100 ml warm distilled water in small portions through the filter. Dry the crucible with ethyl alcohol, wash solution and diethyl ether, as previously directed, and reweigh. The difference in the mass before and after the distilled water treatment represents the mass of the sodium zinc uranyl acetates.

Iron (IS, 2019)

Atomic Adsorption Spectrophotometer was used to find out the concentration of Iron, in the effluent water sample.Sets of standard and effluent iron solutions were taken in 100 ml volumetric flasks containing 1.00, 2.00, 4.00, 5.00, 6.00, 7.00 and 8.00 m. The solution is diluted with 1% HCl solution.

The wavelength for Fe [using 248.3 nm]. Slit width was set at 0.2 nm and the wavelength was maximized. Calculate the percentage metal in the unknown sample.

RESULTS AND DISCUSSION

Physico- chemical parameters are used to evaluate the quality of water. Usually dyes have a synthetic origin and complex aromatic molecular structure which makes them more stable and difficult to biodegrade.

Table 1. Physico-chemical characterization of textile effluent before and after treatment with crab shell chitosan in comparison with maximum allowable concentration values according to TNPCB, BIS and WHO

Quality Indicator	Units	Before treatment	After treatment	Permissible Limits			Percentage of removal
				ATNPCB	BBIS	CWHO	
Colour	Hazen	2790	1880	NM	Pt^{s}-Co scale	Pt^{15}-Co scale	32.61
Total Solids	mg/l	30562	2758	NM	NM	NM	90.97
Total Dissolved Solids (Evaporation)	mg/l	30418	2498	2100	500	1000	91.81
BOD (3 Days)	mg/l	674	258	30	NM	NM	61.72
Chemical Oxygen Demand (COD)	mg/l	2046	907	250	NM	NM	55.66
Total alkalinity	mg/l	4390	370	NM	NM	NM	91.57
Total hardness	mg/l	610	330	NM	NM	NM	45.90
Chlorides	mg/l	10496	340	1000	250	250	96.76
Sodium	mg/l	2315	770	NM	NM	200	66.73
Sulphates	mg/l	3885	747	1000	200	400	80.77
Iron	mg/l	3.46	0.18	NM	1	0.3	94.79

Colour

In the present work, colour of the raw textile effluent was found to be 2790 mg/l and for the treated effluent it was 1880 mg/l which indicates 32.61% colour removal. Likewise, Upadhye and Joshi (2012) reported the colour of textile effluent as 50-2500.

TS and TDS

The total solids and total dissolved solids of raw effluent were 30562 mg/l and 30518 mg/l respectively, which was far above the permissible limitsfor discharge of trade effluents into inland surface waters fixed by TNPCB, BIS and WHO. Kehinde and Aziz, (2014) reported Total Solids of textile waste water as 6000-7000 mg/l. In another study, bleaching of textile waste water shows 2300-14400 mg/l and during dyeing process 500- 14100 mg/l Total Solids was present in textile waste water (Carman and Daniela, 2012). Mohabanci *et al.* (2011) reported TDS of the effluent as 1340 mg/l. Likewise, Eswaramoorthi *et al.*, (2008) reported 8000- 12000 mg/l for TDS of textile effluent. The effluent has high TDS which increases salinity in the water (Kolhe *et al*., 2011). TDS is composed of carbonates, bicarbonates, chlorides, phosphates, nitrates of calcium, potassium and other particles. After treatment, TS and TDS were obtained as 2758 mg/l and 2498 mg/l and the percentage reduction was90.97% and 91.81% respectively.

BOD and COD

The BOD and COD values of the raw effluent were 674 mg/l and 2046 mg/l respectively. The biological oxygen demand was also higher against the TNPCB discharge limit of 30 mg/l. The chemical oxygen demand was higher than 250 mg/l as tolerance limit fixed by TNPCB. In a similar study, Ghay *et al*. (2014) reported BOD of textile effluent as 80-6000 mg/l. Nosheen *et al*. (2000) reported COD value of textile effluentas 180-940 mg/l. BOD depletes dissolved oxygen in water bodies like ponds, lakes, streams and oceans. It affects the aquatic organisms like fishes and also increases anaerobic properties of water. It also acts as the indicator of contamination. After treatment, the BOD was 258 mg/l and COD was 907 mg/l with a percentage of removal 61.72% and 55.66 % respectively.

Total alkalinity and Total hardness

The metallic ions present in water due to the presence of Ca^{2+} and Mg^{2+} and heavy metals such as Fe and Mn dissolved in water is called hardness (Marimuthu *et al.*, 2013). When the hardness of water is high it is unsuitable for drinking, washing and cleaning process. It leads to heart disease and kidney stone formation (Lalitha and Barani, 2004). Increasing levels of carbonates and bicarbonates increases total alkalinity. Total alkalinity increases due to the chemicals like $NaCO_3$, $NaHCO_3$, NaOH, borates, silicates, surfactants and sodium phosphate. In the present work, the total alkalinity and total hardness of the effluent before treatment were 4390 mg/l and 610 mg/l. In a related study Marimuthu *et al*. (2013) reported total hardness of dye effluent as 600 mg/l. After treatment, total alkalinity was reduced to 370 mg/l and reduced total hardness as

330 mg/l. The percentage reductions were 91.57 mg/l and 45.90 mg/l respectively.

Chlorides, sodium, sulphates and iron

The chlorides, sodium, sulphates and iron content of the raw textile effluent were 10496 mg/l, 2315 mg/l, 3885mg/l and 3.46 mg/l respectively. Likewise, Nosheen *et al.* (2000) reported that the chloride content of textile effluent varied between 1140-2650ppm. Sodium content of effluent was very high when compared to the permissible limits. Too much sodium is identified as a risk factor of blood pressure. High sodium content is unfit for crop production and also it deteriorates soils. In a similar work, Eswaramoorthi *et al*. (2008) reported sulphates present in waste water was 600-1000 mg/l. Iron exceeded the discharge limits of BIS and WHO which were 1 mg/l and 0.3 mg/l respectively. Chloride content of textile waste water was 100-6000 mg/l (Kalra *et al*., 2011). High chloride content increases TDS and salty taste and blood pressure (Paul *et al*., 2012). According to TNPCB, BIS and WHO, the maximum permissible limit of chloride content was 1000 mg/l, 250 mg/l and 250 mg/l respectively. The effluent treated with chitosan showed 340 mg/l, 770 mg/l, 747 mg/l and 0.18 mg/lfor chlorides, sodium, sulphates and iron respectively. The reduction percentage were 96.76, 66.73, 80.77 and 94.79 respectively.

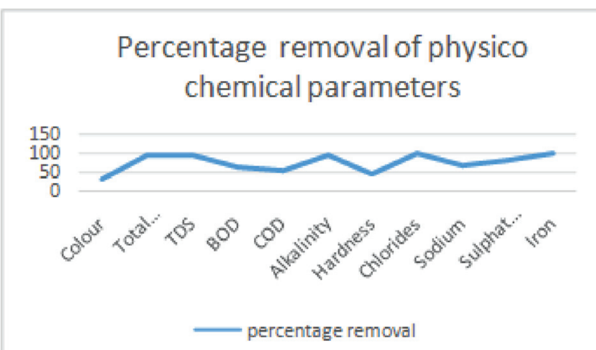

Fig. 1

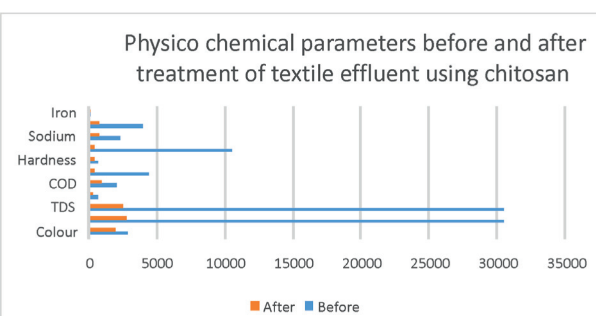

Fig. 1

CONCLUSION

The results from the present investigation showed that the textile dye was highly toxic and chitosan produced from crab *(Portunus sanguinolentus)* could be a good adsorbent for reducing colour, total solids, TDS BOD, COD, total alkalinity, total hardness, chlorides, sodium, sulphates and iron present in the textile effluent.

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