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# **Biodecolourisation of Textile Dye Effluent Using Eggshell**

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# ABSTRACT

Effluents from dyeing units, textile and paper industries contain colour and when such effluents are discharged into the environment they cause damage to natural resources. Hence the present study was undertaken to remove colour using eggshell. After collection of textile dye effluent, physico-chemical properties were analysed before and after treatment. In 10, 20, 30 and 40% effluent, absorbance was monitored at 570 nm and the decolourisation activity was calculated. HPLC analysis was also carried out before and after treatment of effluent. Two way analysis of variance (ANOVA) was carried out for decolourisation activity with the variables, effluent concentration and treatment time period. The treatment of effluent with eggshell was able to reduce total dissolved solids, pH, total hardness, total alkalinity, calcium, magnesium, iron, nitrates, chlorides and phosphates along with colour. HPLC analysis also confirmed the disappearance of certain compounds. Compared to other bioproducts, eggshell can be effectively used in the treatment of textile dye effluents. Eggshell is a waste material from poultry industries and hence it can be used in effluent treatment in an ecofriendly and economic manner.

Key words: Adsorption, dyes, eggshell, low-cost adsorbents, wastewater treatment

# INTRODUCTION

Textile industries are one of the most important and very old industries existing in all over the world which take part for a crucial responsibility in financial prudence of numerous countries. On the other hand, they exploit enormous quantity of water for processing and also liberate them in huge amount in impure state into the environment. The wastewater holds extreme colour as well as elevated level of pollutants. Hence, necessary measures have to be taken before disposal into the environment<sup>1,2</sup>. Reverse osmosis, ion exchange, precipitation, electro-dialysis and adsorption are certain approaches accessible for the elimination of contaminants in industrial effluent<sup>3</sup>. Adsorption was mainly used in effluent management when compared with other methods due to its high efficiency and ease in large scale processes<sup>4</sup>. Activated carbon was the best adsorbent for the removal of several compounds from wastewater<sup>5</sup>. In spite of this, high price of activated carbon has prompted research in developing cheap alternatives to replace activated carbon. Natural materials, biosorbents, waste materials from industry and agriculture were accepted as low-cost adsorbents after extensive research. Some of the adsorbents from bioresources like, eggshell, bagasse, maize cob, feathers, rice husk, coconut shell, chitosan, peat, biomass and algae, industrial wastes like, waste carbon slurries, metal hydroxide sludge and others like, bentonite, kaolinite, zeolites, silica beads, alunite, perlite, starch, cyclodextrin and cotton have been tried for removing dyes and ions from wastewater<sup>6-13</sup>. Around 11% of the total weight of egg was the eggshell<sup>14</sup>. In food manufacturing and restaurants, more amount of egg was used and the eggshells were dumped as waste. In commercial production of egg products, about 28% of produced eggs were broken during processing operations<sup>15</sup>. The eggshell byproducts that were produced at the end of breaking operations constitute the major part in eggshell disposal and they are disposed in landfills without any proper treatment. Due to high level of nutrients like calcium, magnesium and phosphorus, eggshell waste was applied as a fertilizer or feed additive<sup>16</sup>. For waste management, several attempts were done to find out the possible utilization of eggshells<sup>17,18</sup>. Hence in the present work, an attempt was made to test the potential of eggshell in the decolourisation of textile dye effluent.

# **MATERIALS AND METHODS**

**Sample collection:** The textile dye effluent was collected from the textile dyeing unit at Avaniapuram, Madurai district, Tamil Nadu, India. The sample was brought to the laboratory of PG and Research Department of Zoology, The American College, Madurai for analyzing the physical and chemical parameters like, Total Dissolved Solids (TDS), pH, Total Hardness (TH), Total alkalinity (TA), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), nitrates (NO<sub>3</sub>), chlorides (Cl) and phosphates ( $PO_4$ ).

**Collection of eggshell wastes:** Eggshell wastes were collected from the ladies hostel of the American College, Madurai, Tamil Nadu, India and washed thoroughly using distilled water. They were dried in a hot air oven and ground to get smaller particle size.

**Preparation of test solution:** The 10, 20, 30 and 40% of the textile dye effluent concentrations were prepared for both 100 and 1000 mL.

**Decolourisation study:** The eggshell powder was introduced into the textile dye effluent for decolourisation study. Initial absorbance was measured and the solution was observed periodically.

**Estimation of absorbance:** The samples were taken in a cuvette and placed in the UV spectrophotometer. The

absorbance was noted periodically at a time interval of 48 h at the wave length of 570 nm.

**Decolourisation assay:** The decolourisation activity was expressed as percentage decolourization by monitoring the decrease in the absorbance. Decolourization activity was calculated using the following equation.

Decolourisation activity (%) = 
$$\frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100$$
(1)

**High Performance Liquid Chromatography (HPLC) analysis:** The sample containing 10% concentration of textile dye effluent was subjected to HPLC analysis before and after treatment.

**Statistical analysis:** Two ways analysis of variance (ANOVA) was used for the dye effluent with the variables treatment period and dye concentration with significant variation of p<0.05 by applying Microsoft excel package (2016 version).

#### **RESULTS AND DISCUSSION**

The textile dyeing industries are one of the major polluting industries in the world. The uniqueness of discharging textile wastewater varies based on the nature of chemicals used and processing strategies. The physical and chemical characteristics including BOD, COD, odor and color of the effluent have an effect on the environment<sup>19</sup>. Dyes add color to the effluent and are responsible for the disorders, haemorrhage, skin ulceration, nausea, irritation of skin and dermatitis<sup>20</sup>. Thus, it is mandatory to treat the industrial effluent before its disposal into the environment using appropriate strategies. In the present work, the eggshell was tested for its adsorption capacity in the treatment of textile dye effluent. The textile dye effluent exhibited certain parameters that exceed the permissible limits. These physicochemical parameters of the textile dye effluent showed significant reduction after treatment with egg shell as shown in Table 1. Eggshell can remove heavy metal ions and also has a good neutralization capacity in treating effluent<sup>21</sup>. The effluent showed maximum absorption at 570 nm. The absorbance was noted in various experimental concentrations at regular intervals. The variations in absorbance values after decolourisation are shown in Fig. 1.

There was a steady decline in the absorbance as the treatment period increased. This was due to saturation of active sites which prevented further adsorption<sup>22</sup>. Adsorption and ion

Table 1: Physico-chemical properties of textile dye effluent before and after treatment with eqg shell

		Permissible	Egg shell	
		limits	Untreated	treated
Sr. No.	Parameters	(as per TNPCB*)	effluent	effluent
1	TDS (mg L <sup>-1</sup> )	5000-2000	3150	520
2	рН	7.0-8.5	7.43	7.25
3	TH (mg L <sup>-1</sup> )	200-600	1000	250
4	TA (mg L <sup>-1</sup> )	200-600	660	140
5	Ca (mg L <sup>-1</sup> )	75-200	120	64
6	Mg (mg L <sup>-1</sup> )	30-150	168	22
7	Fe (mg $L^{-1}$ )	0.1-1.0	0.19	0.16
8	$Mn (mg L^{-1})$	0.05-0.5	0	Nil
9	NO <sub>3</sub> (mg L <sup>-1</sup> )	45-100	21	4
10	Cl (mg L <sup>-1</sup> )	200-1000	1200	350
11	PO <sub>4</sub> (mg L <sup>-1</sup> )	Nil	0.26	0.22

\*TNPCB: Tamil Nadu Pollution Control Board, TDS: Total Dissolved Solids, TH: Total Hardness, TA: Total Alkalinity, Ca: Calcium, Mg: Magnesium, Fe: Iron, Mn: Manganese, NO<sub>3</sub>: Nitrates, CI: Chlorides, PO<sub>4</sub>: Phosphates



Fig. 1: Effect of egg shell treatment on the decolourisation of textile dye effluent

exchange are the major factors influencing decolourisation. Dye concentrations, dose of the adsorbent and contact time are the significant parameters to analyse in adsorption studies. The adsorbent dose decides the capacity of the adsorbent for a specific dye concentration during specific contact period<sup>23</sup>. In the present study, removal of dye in 10, 20, 30 and 40% textile effluent concentrations by eggshell was studied during different contact time periods (0, 2, 4, 6, 8 and 10 days). The dye removal activity of eggshell varied depending upon the dye effluent concentration and contact time (Fig. 2). The amount of dye adsorption by eggshell decreased with the increase in textile dye effluent concentration. Eggshell was found to decolourise effectively in the lowest effluent concentration (10% of dye effluent). The adsorption sites available were very less at high concentration. Thus, the percentage of dye removal is always based on concentration<sup>24</sup>. Figure 2 also shows increase in removal efficiency with increase in contact time between adsorbate and adsorbent. It



Fig. 2: Decolourisation activity of egg shell on textile dye effluent

can be mentioned that more time becomes available for the textile dye to make an attraction complex with egg shell. Here, removal percentage is increased steadily over the treatment period of experiment. It is concluded that textile dye and eggshell should be in contact for ten days in order to get maximum removal percentage. High performance liquid chromatography (HPLC) is a reliable analytical tool in biodegradation studies. The appearance of new peaks at different retention times along with disappearance of major peaks when compared with the original dye is an indicator of biodegradation and formation of certain new compounds<sup>25</sup>. In the present study, HPLC analysis of the untreated 10% textile dye effluent exhibited several peaks but after treatment with eggshell, these peaks were replaced by new peaks indicating biodegradation.

The results of HPLC analysis clearly indicated the degradation of textile dye effluent by eggshell. After incubation under static conditions, alterations in the pattern of peaks of eggshell treated sample was observed when compared to untreated sample. It is thus rational to propose that these peaks represent degradation of the textile dye effluent. The HPLC profile of the untreated sample showed major peaks at retention time 2.437, 2.560, 2.840, 3.800, 4.643, 5.243, 6.230 and 6.450 min (Fig. 3a), while the egg shell treated sample showed peaks having different retention times 2.800, 3.053, 3.933 and 4.813 min (Fig. 3b) than that of the untreated sample. Absence of peaks in treated sample corresponding to the retention time to that of the untreated sample indicated complete biotransformation of the textile dye effluents to other simpler products and confirmed biodegradation of the textile dye by eggshell. This again supports the degradation and also ensures the safer disposal of eggshell treated textile

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Table 2: ANOVA for the effluent concentration and treatment pe	eriod during the decolourisation	of textile dye effluent using egg shell
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Source of variation	SS	df	MS	Calculated F-value	F-table value at 5% level	Level of significance
Concentration	50.756	3	16.9186	2.248353	3.4903	Not significant
Treatment period	10655.95	4	2663.99	354.0223	3.25916	Significant
Residual error	90.299	12	7.52492			
Total	10797.01	19				

SS: Sum of squares, Df: Degree of freedom, MS: Mean Squares, F: Factor



Fig. 3: HPLC analysis of 10% textile dye effluent, (a) untreated and (b) treated using eggshell

effluent into environment<sup>26</sup>. The two way analysis of variance (ANOVA) for the variable, treatment period showed statistically significant variation of p<0.05 in biodecolourisation. The variation due to the textile dye effluent concentration was not statistically significant for the textile dye effluent treated with eggshell (Table 2).

# CONCLUSION

Eggshell is a biowaste material which is easily available at a low cost and can be used as a successful adsorbent in wastewater treatment. The optimization study was carried out under different experimental conditions for the biodecolourisation of textile dye effluent using egg shell. It was found that egg shell decolourised effectively in the lowest concentration of effluent. HPLC analysis of the textile dye effluent showed that there was a difference in the retention time of the experiment sample compared to control. From the above study it is clear that eggshell is efficient in the biodecolourisation of the textile dye effluent.

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