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# Preliminary studies on use of Cuttle fish bone as a green biosorbent for treatment of waste waters

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## ABSTRACT

Water is a precious natural resource essential for human life and it is imperative to preserve its quality. Rapid increase in population and industrialization have led to degradation of aquatic resources ultimately affecting human health. Most of the conventional methods used for waste water treatment are inefficient and costly. Hence new economical and eco-friendly methods need to be investigated. Present study envisages the potential use of cuttle fish bone or internal shell of Sepia as an economical and environment friendly, green biosorbent for treatment of waste waters. For comparison, commercial chitin and chitosan – bioactive compounds obtained by processing of shell waste, were also used. Effect of these biosorbents on various physico-chemical parameters of waste-waters were studied. It was found that cuttle fish bone was more effective in treating acidic waste waters while chitin and chitosan were more effective in alkaline conditions.

**Key words:** Cuttlefish bone, Sepia shell, Chitin, Chitosan, Biosorbent, Waste water treatment

## INTRODUCTION

Water has always been at the center of healthy ecosystems and human societies, yet the water resources on which we all depend are becoming increasingly polluted due to dumping of inadequately treated domestic, industrial and agricultural wastes into the water bodies. The contamination of aquatic ecosystems affects humans directly by destroying fisheries or causing other impacts on biodiversity resulting in lower food yield. Many industries release their effluents with various pollutants such as heavy metals, sulphates, phosphates, nitrates, and dyes etc., that have harmful effect on the environment (Priyantha and Bandaranayaka, 2011). The adverse effects due to heavy metal contamination on human are metal fume fever, lung cancers, hypertension, cardiovascular diseases, DNA damages, haemolysis, renal and liver failures, allergies and even gradual death. Eutrophication, on the other hand, is a greater problem in the environment due to the high level of phosphorous and nitrates. Higher nitrogen levels in ground water cause the blue baby syndrome and stomach and gastrointestinal cancers. Diarrhea and some laxative effects may result from sulphate contamination (Kulasooriya, 2014). Therefore industrial effluents must be in an acceptable condition before they are discharged into natural water bodies so as to avoid their adverse effects on human being, animals and plants.

Considering above facts, Central Environmental Authority (CEA) has enforced standard limits to release industrial effluents to the environment. These standards limits are on basic water quality suspended solids (TSS), Chemical oxygen demand (COD), Biological oxygen demand (BOD), nitrate, sulphates, phosphates and heavy metals are some of the key parameters. In order to remove these substances various physical, chemical and biological treatment methods are used in industries. Many physicochemical methods like coagulation, flocculation, ion exchange, membrane separation, oxidation etc. are available for treatment of heavy metals and dyes. But these methods are inefficient, non eco-friendly or costly. Increasing public awareness and concern about the environment as well as stringent laws of waste disposal have led to designing of new, cost-effective, green methods for treatment of waste waters. In this context, biosorption / adsorption using by-products/ waste products from agriculture, sea food and other industries could serve as economically feasible, eco-friendly and sustainable method for treatment of waste waters Natural substances, such as bio-sorbents, coconut shell, brick clay, rice husk, coir dust and saw dust, feldspar and dolomite have been used to remove some heavy metals, anions and dyes from industrial wastewater (Priyantha and Perera, 2001). A review on the removal of metals and dyes by low-cost adsorbents have been presented (Bailey *et al*. 1999; Babel and Kurniawan 2003; Crini, 2006; Ahmed *et al*. 2020; Bhatacharjee *et al*. 2020; Elgarahy *et al*. 2021; Kashir Ali *et al*. 2021),

Sea food processing industry generates tremendous amount of shell waste, disposal of which has become a costly affair, sometimes a source of pollution and health risk (Kaur, 2014). Shell fish waste is classed as a Category 3 animal by product and must be handled and treated according to Animal by Product Regulation if it is destined to go back into food or feed chain. Environmental awareness among the masses and stringent environmental laws stress the need for safe disposal of this waste. Internal shell of Sepia also known as cuttlefish bone is one of the processing discard of sea food processing industry. It is a hard, brittle, internal shell composed primarily of aragonite. Cuttlefish bone is a chambered, gas-filled shell also used for buoyancy Cuttlebones are commonly used as calcium-rich dietary supplements for caged birds (Norman & Reid, 2000) and shell powder is also used as an antacid or as an absorbent.

Shell waste can be profitably utilized for production of bioactive compounds like chitin and chitosan. Chitin is a naturally occurring nitrogen containing polysaccharide related chemically to cellulose poly-β-(1→4)-N-acetyl-D-glucosamine (Austin *et al*., 1981), which is major constituent of the exoskeleton of insects, crustacean and arachnids. Chitosan (poly-β-(1→4)-glucosamine), a derivative of chitin, has attracted the attention of many researchers and industries owing to its antimicrobial activity, biocompatibility and biodegradability Chitin and Chitosan find applications in various field mainly paper making, textiles printing and sizing, flocculation, ion exchange chromatography, removal of metal ions and dyes from industrial effluents, manufacture of pharmaceuticals and cosmetics and as an additive in food industry (Nair, 1994, Mathur *et al*., 1990; Li *et al*., 1992; Muzzarelli, 1997; Percot *et al*., 2003; Kurita *et al*., 2005, Brzeski *et al*., 1987).

Shells of crustaceans and mollusks have been known to improve the water quality by reducing levels of BOD, COD, dissolved and suspended solids, nitrates and phosphates and heavy metals. Thus utilization of shell waste for waste water treatment could be an environment friendly and economical method of shell disposal besides providing economic benefits (Kaur, 2014). The modern thinking in the area of waste treatment is increasingly in the area of Symbiotic relations i.e. using of waste of one industry by another which in turn benefits both. As a global community, we need to refocus our attention on improving and preserving the quality of our water..

## MATERIAL AND METHOD

**Waste water sample collection:** Effluent from chemistry laboratory of an undergraduate science college was collected and used as Waste water sample from Chemistry Lab (L).

Effluent from a Jean dyeing unit at MIDC, Ambernath, and Mumbai was collected and used as Waste water sample from Dye industry (D).

**Preparation of biosorbent:** Cuttlefish bone or internal shells of Sepia were collected from sea food processing unit at Taloja, Mumbai. The shells were thoroughly washed, dried and pulverized with mortar and pestle and stored in air tight container at room temperature. Commercially available Chitin and Chitosan were purchased from Otto. Chitosan had following specifications – moisture <10%, pH 7-9, viscosity <200 cps, degree of de-acetylation >80% and these were used in the experiment for comparative purpose.

**Treatment and Analysis of Waste water samples:** One gm. of powdered shell / chitin / chitosan were added per 100ml of lab and dye waste water samples and kept at room temperature. Various physico-chemical parameters viz. pH, phosphate, nitrate, nitrite, absorbance and heavy metals like Cu, Zn and Pb were estimated in the samples using standard methods (APHA, 1999). The above-mentioned parameters were analyzed in triplicate for treated and untreated (control) samples after 15 days of interval.

## RESULTS and DISCUSSION

Percentage Reduction of Physico-chemical parameters w.r.t. Control samples in Treated Lab and Dye samples was calculated and tabulated as well as illustrated in form of Graphs (Table 1 and 2; Fig. 1 and 2). Addition of Cuttle fish bone /Sepia shell, chitin and Chitosan raised the pH of the Lab effluent from 0.5 to 4.67, 1.6 and 1.4 respectively and that of Dye effluent from 6.8 to 8.3, 8.4 and 8.6 respectively. The increase in pH by addition of chitin and chitosan was less as compared to sepia shell powder in lab sample.

In lab samples, cuttle fish bone/ sepia shell was very effective in removal of hardness (58.9 %), phosphate (57.4 %), nitrate (59.99 %), nitrite (19.98 %) and absorbance (50.0%) whereas chitin and chitosan were effective only in reducing hardness by 22.36% and23.2% respectively. Also, chitin reduced the absorbance value by 8.5% in the lab sample. In Dye samples, chitin and chitosan respectively were effective in reducing phosphate (0% & 21%), nitrate (47.8% & 56.5%), nitrite (44.46% & 55.5%), and absorbance (40% &56.66%) whereas sepia shell reduced only nitrite (55.42%) and absorbance (20.0 %). Fatma E. Farghaly et. al, (2015) treated industrial wastewater by squid bones (cuttlebone) as a carbonate mineral. The average removal percentages for COD, TSS, TKN and heavy metals were 94%, 95%, 85% and 95%, respectively.

Internal shell of sepia/ cuttle fish bone is porous and made of aragonite Sepia pens have been found effective for color/ dye removal from textile wastewaters (Figueiredo *et al*, 2005; Farzana, MH and Meenakshi, 2014). In the present study sepia shell reduced the absorbance levels in the lab and dye samples by 50% & 20% respectively.

In lab sample, addition of cuttle fish bone/ sepia shell powder resulted in 90% reduction in Zn level and 81.8% reduction in Pb level. However, Zn and Pb showed reduction of 50% and 9% respectively by both chitin and chitosan. Copper level reduced by 26.8% only in the case of chitosan (Table-1; Fig. 1). In case of dye sample, chitin and chitosan effectively reduced the levels of Cu (50%), Zn (97%) and Pb (40% &60% respectively) whereas sepia shell was effective only in decreasing levels of Zn (88 %) (Table – 2; Fig. 2).

**Table 1 - % Reduction of Physico-chemical parameters in Treated Lab samples**

| | Cuttlefish bone | Chitin | Chitosan |
|---|---|---|---|
| **Hardness** | 58.91 | 23.2 | 23.20 |
| **Phosphate** | 57.14 | 0.00 | 0.00 |
| **Nitrate** | 59.99 | 0.00 | 0.00 |
| **Nitrite** | 19.98 | 0.00 | 0.00 |
| **Absorbance** | 50.00 | 8.50 | 0.00 |
| **Cu** | 0.00 | 26.80 | 26.80 |
| **Zn** | 90.00 | 50.00 | 50.00 |
| **Pb** | 81.80 | 9.00 | 9.00 |

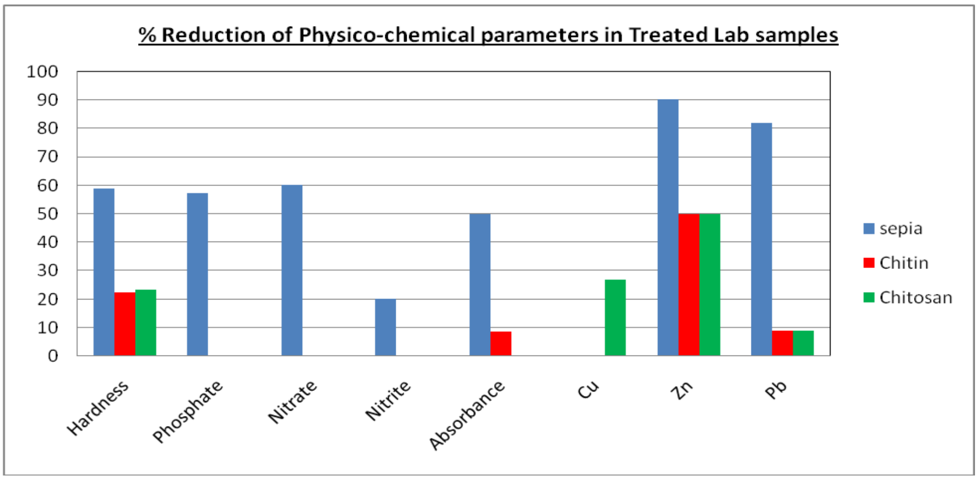


**Figure 1 – Percentage Reduction of Physico-chemical parameters in treated Lab samples**

**Table 2: % Reduction of Physico-chemical parameters in Treated Dye samples**

| | **Cuttlefish bone** | **Chitin** | **Chitosan** |
|---|---|---|---|
| **Hardness** | 0.00 | 0.00 | 0.00 |
| **Phosphate** | 0.00 | 0.00 | 21.00 |
| **Nitrate** | 0.00 | 47.8 | 56.50 |
| **Nitrite** | 55.42 | 44.46 | 55.50 |
| **Absorbance** | 20.00 | 40.00 | 56.66 |
| **Cu** | 0.00 | 50.00 | 50.00 |
| **Zn** | 88.00 | 97.20 | 97.20 |
| **Pb** | 0.00 | 40.00 | 60.00 |

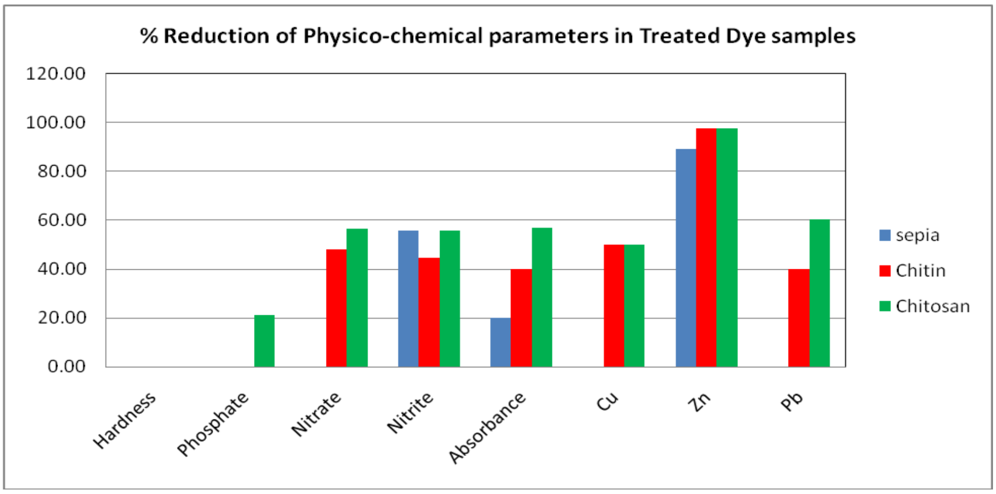


**Fig. 2 – Percentage Reduction of Physico-chemical parameters in treated Dye sample**

Chitin and chitosan have been utilized as attractive source of adsorbents, especially for metal removal. McKay *et al.* (1989) have observed the adsorption capacity of chitosan for removal of $Hg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Zn^{2+}$as 815, 222, 164, and 75 mg/g, respectively. Wu *et al* (2001) have reported that besides metals, the reactive dyes could be removed from aqueous solution using chitosan as adsorbent. Fatma E. Farghaly et. al, 2015 found the order of adsorption capacity of squid bones for metal ions was as follows: Hg2+ > Pb2+ > Cd2+.

The presence of heavy metal ions and dyes in the environment is of major concern due to their toxicity to life. With better awareness of the hazards associated with heavy metals and synthetic dyes a number of technologies have been developed for the removal of these pollutants from waste water system. However, the process of adsorption is considered as one of the most appropriate methods for this purpose. The ability of certain types of inactive, dead, biomass to bind and accumulate heavy metals from aqueous solutions through non-metabolically mediated or physico-chemical pathways of uptake is known as Biosorption (Volesky, 1990). The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent, and the possibility of adsorbate recovery (Veglio *et al* 1997, Elgarahy *et al*. 2021).

Chitin from squid pens has β–structure which is different from α–structure of crustacean chitin. The polymer chains of α –structure have strong intermolecular hydrogen bonding. While β–chitin has weak inter molecular interaction, but the β–chitin has greater reactivity to the deacetylation and chemical modification than α–chitin, (Ausa, *et al*., 2004). Chitosan is a polysaccharide compound (2-amino-2deoxy-D-glucose), which is mostly obtained from deacetylation of chitin, a poly (N-acetyl-D-glucosamine) (Minamisawa *et al*., 1999). Chitosan is able to be dissolved in an acid solution medium below pH 6 by the interaction between hydroxyl (-OH) and amine (-NH2) groups (Li *et al*., 2004). Therefore, chitosan shows a very high adsorption ion through several mechanisms including; chemical interaction, such as chelation, electrostatic interaction, as well as ion exchange, or the formation of ion pairs (Jeon *et al*., 2005).

## CONCLUSION:

Sustainable wastewater treatment is one of the foremost challenges of twenty first century. With the ever increasing contaminants being dumped in the water bodies, finding eco-friendly and affordable treatment options will remain a priority, especially for developing countries. Adsorption is one of the most researched and used method for removing dyes and heavy metals from wastewater.s, termed as Biosorption ie. adsorption using living and non-living biomass, has gained attention in the last two decades due to promising results. Cuttle fish bone/ Sepia shell and other bioactive compounds like chitin and chitosan derived from the shell waste have the potential to serve as non- conventional, low cost, green biosorbents. pH plays a significant role in metal adsorption. Sepia shell is more effective in improving water quality under acidic conditions whereas chitosan is more effective under alkaline conditions. These methods can be adopted even in combination with other treatment technologies which will help to keep the resilience of healthy environment for future generations as well.

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**Conflicts of Interest**: The authors declare no conflict of interest.

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