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# A review on role of Molluscan shells in the removal of pollutants from aquatic water bodies

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**ABSTRACT**

Water pollution is a topic of great concern worldwide and the major contributing factors to it is the heavy metal discharge from various industries. Heavy metals being non-biodegradable in nature have long lasting effect on our ecosystem as they bioaccumulate in various organisms through the process of biomagnification. These heavy metals not only affect the flora and fauna but also human beings. Most of the heavy metals being carcinogenic have adverse effects on human health. Therefore, it is important to remove these heavy metals from aquatic ecosystem. Though, various methods for metal removal such as precipitation, evaporation, ion exchange, membrane processes, electroplating etc. are in use nowadays but all of these have some disadvantages. Thus, there is a need for more efficient and sustainable method for waste water treatment. Biosorption could be considered as a highly efficient and economical way to remove these toxic loads from water bodies. This paper reviews the use of molluscan shell as bio sorbent for industrial waste water treatment.

***Key words :*** *Biosorption, Heavy metals removal, Molluscan shells, Water treatment.*

## Introduction

Water pollution is one of the greatest challenges faced by the global society. Increasing industrialization and urbanization has resulted in discharge of untreated toxic pollutants into the water bodies. The pollutants entering the water bodies contain various organic, inorganic, heavy metals, degradable and non-degradable matter etc. Among the various kinds of pollutants, heavy metals are the most common and are considered to be serious contaminants of aquatic ecosystem. Heavy metals are defined as those metals which have specific density of above 5 g/cm$^3$ (Alissa *et al*., 2011). Heavy metals in less concentration are essential for normal body functioning. Some heavy metals like Cobalt, Zinc, Copper, Iron, Manganese, etc. acts as catalysts for various enzymatic activities within our body. But according to WHO (1993), some heavy metals are not normally a part of the human body and are toxic. These includesArsenic, Cadmium, Copper, Cobalt, Chromium, Lead, Mercury, Nickel, Zinc etc. As these metals are not biodegradable, they tend to accumulate in aquatic biota leading to its biomagnification which causes health hazards in human beings and other living organisms (Weerasooriyagedra and Kumar, 2018). In humans, they may cause many diseases and disorders such as nausea, headache, vomiting, skin irritation, kidney failure, liver failure, hypertension and disorders of brain which ultimately threaten human life. Chronic exposure to these heavy metals can be carcinogenic and may lead to various cancers.

The main source of heavy metal origin are batteries industries, automobiles industries, chemical industries (pesticides, fertilisers etc.), paint industries, alloy industries etc. (Ahalya *et al*., 2003). These industries discharge waste water containing various toxic metals either directly or indirectly into nearby water resources.

Though number of techniques for removal of heavy metals from contaminated watersuch as chemical oxidation, precipitation, ion exchange, reverse osmosis and membrane separation (Wang and Chen, 2006) are in use, but all of them are very costly, produce huge amount of sludge and secondary pollutants which are economically expensive to digest. Therefore, there is a dire need of some cost efficient and eco-friendly method for treating waste.

Recently, biosorption has emerged as a new and effective technique for removal of heavy metals from contaminated waste water generated from various industries. It has many advantages over other traditional technologies like low operating cost, eco-friendly and high efficiency for removal of heavy metals (Volesky and Holan, 1995). Biosorption is a property of certain types of inactive, dead or microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution (Gadd, 2009). This physical process involves a solid phase (sorbent) and a liquid phase (solvent) containing dissolved metal ions (sorbate) (Ahalya *et al*., 2003).

Earlier, many biosorbent materials such as algae, bacteria, agricultural by-products including wheat bran, rice husk, sugarcane bagasse, soya bean hull, cotton seed hulls, straw, corn cobs, neem bark, almond shell, peanut shell, green coconut shell etc. have been investigated by a number of workers (Das *et al*., 2008 and Mathew *et al*., 2016) but very less work has been done on using aquatic animals as biosorbent material. It is also known that very few organisms can be used as biosorbent such as molluscs shell, crab shell and sponges. In this paper we shall focus on molluscan shell as biosorbent material.

Molluscs represent one of the most diverse and second largest Phylum of the Animal Kingdom after Arthropods. Being more diverse, they occupy a vast range of habitat including both aquatic and terrestrial ecosystems. Shell of molluscs have high porosity and is made up of 95%-99% calcium carbonate and rest 1-5% consists of protein (Kalpan, 1998). The microstructure of molluscan shell reveals that it mainly consists of calcite as well as aragonite and act as a natural ceramic with great strength and hardness (Boro *et al*., 2012). Due to chemical composition of their shell, they can be used in the treatment of waste water. In a solution, calcium present in the shell gets dissociated into calcium ion and various other calcium complexes such as calcium hydroxide ion. These positively charged ions combines with negative charge forming colloidal particles, which ultimately adhere on the bioadsorbent (Jatto *et al*., 2010).

The main objective of this review article is to promote the research work on using low cost and highly efficient molluscan shell for removing heavy metals and other pollutants from waste water. To do so various physiochemical and other factors influencing the process of adsorption such as pH, temperature, contact time, size of adsorbate, concentration of adsorbent and adsorbate are reviewed.

## Materials and Methods

### Preparation of molluscan shell

The collected molluscan shells should be thoroughly cleaned with distilled water so as to remove debris and algae. They should be dried in the sunlight for at least two days before crushing them into fine particles. The crushed shell particles should then be passed through different mesh sized sieves to obtain homogenous particle size. Later on, these homogenized particles must be dried at 105 °C in oven for 1 hour and stored in zip lock poly bags at 4°C till further use (Darmokoesoemo *et al*., 2016).

### Biosorption experiment for removal of heavy metal

The experiment should be carried out using glass troughs containing either waste water or prepared heavy metal solution. To this desired amount of shell dust must be added. The concentration of heavy metals must be noted by using atomic adsorption spectroscopy (AAS) both before and after the addition of shell dust, so as to calculate the removal efficiency of heavy metals by the mollusc shells using the following formula given by Weerasooriyagedra and Kumar (2018):

$$Q=C_0-C_1/C_0$$

In which, Q represents removal efficiency of specific metal in percentage

$C_0$ represents initial concentration of heavy metal in mg/L

$C_1$ represents final concentration of heavy metal in mg/L

### Physico-chemical analysis

All the physico-chemical parameters should be performed according to standard methods (APHA, 1992 and Adoni, 1985).

### Research findings in physiochemical parameters of waste water after treatment with molluscan shell dust

Jatto *et al*. (2010) used *Achatina* shells for the treatment of waste discharged from food industries so as to study the use of snail shell as an adsorbent for waste water treatment. The waste water was analysed before and after snail shell treatment. According to their work, there was an increase in the pH value of the solution which was due to the presence of calcium carbonate in the shells. Phosphate was completely removed from the treated sample as the calcium ions in the shell have the ability to react with phosphate ion and form calcium phosphate and calcium hydrogen phosphates which can be removed from water by filtration. They observed a decline in the value of Total solids (TS), Total suspended solids (TSS) and Total dissolved solids (TDS) after water treatment. This reduction in both TDS and TSS lead to a drop in conductivity and Tubridy respectively. The decline in concentration of nitrates, sulphates, ammonium – nitrogen, phosphates, BOD, COD while an increase in DO indicating improvement in water quality (Table 1.)

Udeozor and Evbuomwan, (2014) used activated snail shell with $H_3PO_4$ adsorbent for treating beverage industries waste for different intervals of time (10 min, 20 min, 30 min, 40 min). The results were similar to that of the experiment performed by Jatto *et al*. (2010) They too observed a rise in pH and decrease in turbidity, conductivity, TSS, TDS, TS, BOD, COD, nitrates and sulphates. Phosphates were almost completely removed. The increase in the concentration of dissolved oxygen revealed enhancement in water quality. (Table 2.)

### Research findings in removal of heavy metals from waste water using mollusc shell dust

According to Naik *et al*. (2016) the shell of bivalves, oysters and crabs are known to remove heavy metals such as Mercury, Cadmium, Arsenic, Nickel, Lead, Fluorides and textile dyes from industrial waste due to good adsorbing properties. The findings of Naik *et al*. (2016) validated that crab shell possess 100% removal efficiency while bivalve and oyster shells possess 98% to 99% removal efficiency for all the metals except Arsenic, for which crab and oyster shell powder showed 85% removal and bivalve shell powder showed 91% removal efficiency. The trend of adsorption of heavy metal in descending order was Mercury > Lead > Nickel > Fluorides > Cadmium >Arsenic.

Pre-treatment of molluscan shell with either acid or base has proven to improve efficiency. The adsorption of heavy metals was enhanced on EDTA (ethylene diamine tetra acetic acid) modified snail shell of *Archachatina marginata* (Ikhuoria and Uyammadu, 2001). Activation of snail shell with $H_3PO_4$ increases the surface area and porosity thus improving the adsorption capacity (Udeozor and

**Table 1.** Variations in different physico-chemical parameters of water before and after snail shell dust treatment (Jatto *et al.*, 2010)

| Parameters | Unit | Result before treatment | Results after treatment |
|---|---|---|---|
| pH | - | 5.42 | 6.42 |
| Colour | - | Dark Brown | Light Brown |
| Turbidity | NTU | 332 | 133 |
| Temperature | $^{o}C$ | 20 | 20 |
| Conductivity | $Mscm^{-1}$ | 0.294 | 0.164 |
| Total suspended solids | mg/L | 0.814 | 0.184 |
| Total dissolved solids | mg/L | 15600 | 15200 |
| Total solid | mg/L | 15600.8 | 15200.02 |
| Ammonium nitrogen | mg/L | 0.085 | 0.015 |
| Nitrates | mg/L | 41.08 | 13.32 |
| Sulphates | mg/L | 58.11 | 15 |
| Phosphates | mg/L | 0.173 | 0.00 |
| DO | mg/L | 1.14 | 2.16 |
| BOD | mg/L | 29.27 | 19.77 |
| COD | mg/L | 872 | 215 |

Evbuomwan, 2014). According to Liu *et al.* (2009) acid pre-treated Bivalve molluscan shells were more efficient than raw untreated shell. In contrary to this Naik *et al*. (2016) suggested that metal adsorbed by base digestion of adsorbent show more adsorption capacity than acid digestion.

**Factors affecting adsorption**

The adsorption of heavy metal varies with many factors such as pH, initial metal ion concentration, initial concentration of adsorbent, temperature, size of adsorbent and contact time.

**Effect of pH on adsorption**

It is known that precipitation of heavy metals occurs at high pH and at low pH due to protonation the metal adsorption capacity decreases. In accordance with the findings of Hossain and Aditya (2013) the adsorption of cadmium by *Physaacuta* shell dust showed less adsorption at pH 2 but with an increase in pH, the absorption also increased and maximum adsorption was found to be at pH of 6. Subsequently, there was slight decline in adsorption on further rise in pH (Fig. 1). However, Al-Saeedi *et al*., (2019) found that 50% removal of lead was obtained at pH 2 and at pH 7 maximum lead removal percentage of 94.5% was observed which decreased to 92.9% at pH 8.

**Effect of initial metal ion concentration**

Heavy metal adsorption increases with increase in the metal ion concentration of solution. According to Hossain and Aditya (2016), at 25 mg/l Cadmium ion concentration shows less adsorption while at 800mg/l it shows maximum adsorption after which adsorption remains same. (Fig. 2.)

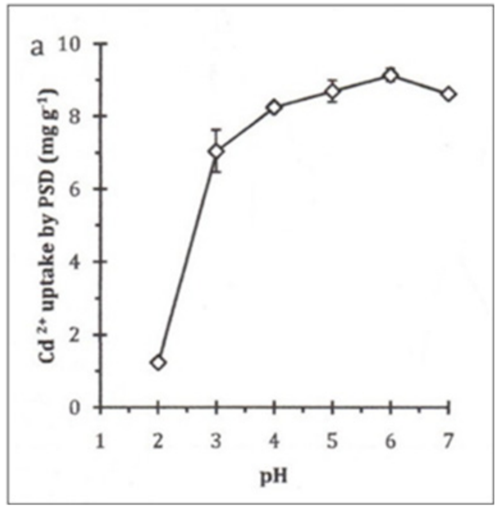


**Fig. 1.** Variation in cadmium uptake by *Physaacuta* shell dust with pH (Hossain and Aditya, 2013)

**Effect of initial concentration of adsorbent**

With the increase in the initial concentration of adsorbent the process of adsorption also increases due to more availability of binding site or active site for heavy metals. As shown in Fig. 3, the percentage removal of nickel ion with increase in adsorbent dosage led to removal of 70% of nickel ion but further increase in adsorbent dosage showed slow increase (Al-Saeedi *et al*., 2019). As per the study conducted

**Table 2.** Variation in various physiochemical parameters before and after treatment at different time interval (Udeozor and Evbuomwan, 2014)

| Parameters | Units | Raw water sample | Treated water sample (time) | | | |
|---|---|---|---|---|---|---|
| | | | 10 mins | 20 mins | 30 mins | 40 mins |
| Ph | - | 10.2 | 8.9 | 8.6 | 8.1 | 7.8 |
| Colour | - | Brown | Clear | Clear | Clear | Clear |
| Turbidity | FAU | 41 | 9 | 6 | 3 | 1 |
| Temperature | °C | 30.3 | 29.7 | 29 | 27.8 | 26.2 |
| Conductivity | μs/cm | 342 | 176 | 164 | 158 | 144 |
| TSS | mg/l | 0.287 | 0.12 | 0.088 | 0.076 | 0.041 |
| TDS | mg/l | 641 | 567 | 532 | 493 | 487 |
| TS | mg/l | 641.287 | 567.12 | 532.088 | 493.076 | 487.041 |
| BOD | mg/l | 48 | 22 | 16 | 12 | 10 |
| COD | mg/l | 146 | 46 | 44 | 39 | 37 |
| DO | mg/l | 1.8 | 3.2 | 3.8 | 4.03 | 4.98 |
| Nitrates | mg/l | 5.12 | 1.15 | 1.08 | 1.03 | 0.97 |
| Phosphates | mg/l | 0.066 | 0.013 | 0.005 | 0.0012 | 0 |
| Sulphates | mg/l | 116.42 | 32 | 28 | 24 | 22 |

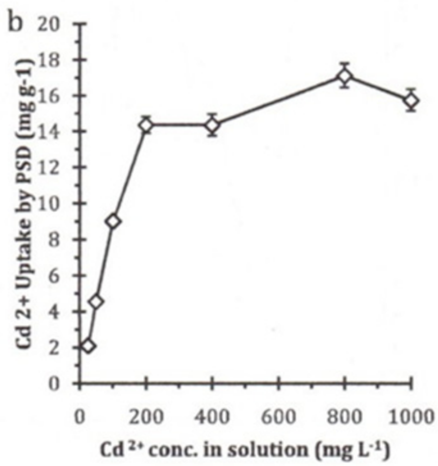


**Fig. 2.** Relation between different initial concentration and amount of Cadmium uptake by *Physaacuta* shell dust (Hossain and Aditya, 2013)

by Shahzad *et al*., 2017 out of 5 mg/l, 10 mg/l and 15 mg/l, maximum adsorption occurred at 15 mg/l which also depicted that the process of adsorption increases with an increase in concentration of adsorbent.

### Effect of temperature on the process of adsorption

Temperature plays an important role in adsorption. It is believed that increase in temperature results in lesser adsorption and at high temperature process of desorption occurs. According to Fig. 4, raw and treated bivalve mollusc shell show high removal efficiency within temperature range of 15-40% decrease in the biosorption at high temperature occurs due to damage of adsorption site (Liu *et al*., 2009).

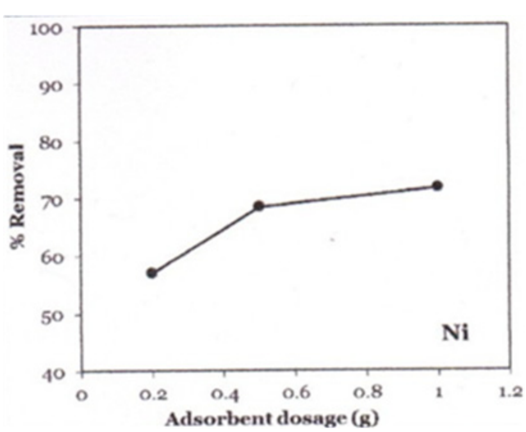


**Fig. 3.** Variation of percentage removal of nickel with different adsorbent dosage (Al-Saeedi *et al*., 2019)

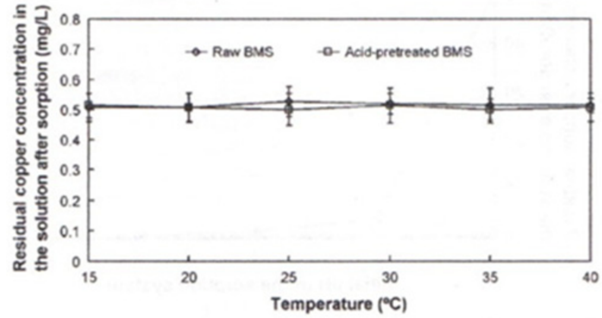


**Fig. 4.** Variation in removal of copper by molluscan shell with temperature (Liu *et al*., 2009)

### Effect of Adsorbent Size on the Process of Adsorption

Adsorbent size is another key factor influencing the process of adsorption. Al-Saeedi *et al*. (2019) found that when large porous material is broken down into smaller size there is increase in surface area leading to availability of more active sites, thus validating that adsorption capacity increases with the decrease in the adsorbent size. They observed that at adsorbent size of 212 µm, removal percentage of Pb (a!) was 94.45% while at 400 µm it was 92.8% (Fig.5).

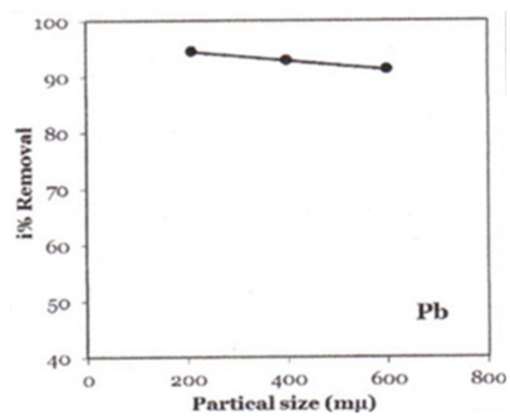


**Fig. 5.** Variation in removal of lead (Pb) with size of adsorbent (Al-Saeedi *et al*., 2019)

### Effect of Contact Time on the Process of Adsorption

Contact time plays a significant role in the process of adsorption. Xu *et al*. (2019) noted that there was steady increment in adsorption until saturation point was reached after which, the process proceeded at constant rate. The amount of heavy metal adsorbed by oyster shell powder was rapid and higher initially till 200 minutes due to sufficient adsorption sites which later on decreased with reduction in available sites for adsorption until saturation point was reached. They further revealed that cadmium and lead reached saturation point in 200 min while copper in 400 min. This is shown in Fig. 6. According to Shahzad *et al*. (2017) the maximum absorption of Pb occurred at 90 min, beyond which equilibrium was attained. Similar findings were also observed by Liu *et al*. (2009) who illustrated that maximum Cu ion was removed at 90 min using bivalve mollusc.

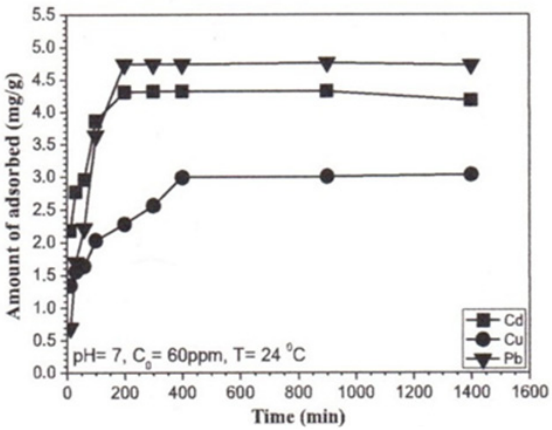


**Fig. 6.** Variation in heavy metals adsorbed by oyster shell powder with different contact time interval (Xu *et al*., 2019)

Combination of two or more than two natural biosorbents can be another method to obtain higher efficiency in reducing heavy metal load from the environment (Weerasooriyagedra and Kumar, 2018). Molluscan shell along with other naturally available biosorbent can be used together. A study conducted by Campangne and Li (2009) to inspect the efficiency of 4.0-4.75 nm crushed shell and Sphagnum peat moss for exclusion of cadmium and nickel ions from binary aqueous solution testified that crushed molluscan shell can be a better filter medium for cadmium while Sphagnum peat moss for nickel removal.

A large amount of molluscan shell waste is produced by pearl industries as well as sea food restaurants which is dumped into nearby landfills causing bad odour. Moreover, dead shells from the sea remain scattered all around the shores polluting the environment. These shell waste can be used as low cost, eco-friendly, highly efficient biosorbent for waste water treatment. This method of treatment does not produce sludge or any secondary pollutants unlike other conventional method of waste water treatment such as chemical oxidation, ion exchange, reverse osmosis, precipitation and membrane separation. Molluscan shells are not only known for removing heavy metals but also removes dyes (Al-Damy *et al*., 2018), fluorides (Naik *et al.,* 2016), sulphates, nitrates (Jung *et al.,* 2007) and for eutrophication control (Kwon *et al.,* 2004). The water obtained after purification can be used for various domestic and agricultural processes and with further treatment water can also be converted into drinking water (Weerasooriya and Kumar, 2018).

Heavy metals can even be recovered back from biosorbent through the process of desorption which involves the use of desorbing agent such as HCl (Castaneda *et al*, 2012). These recovered heavy metals can be used in different industries such as jewellery, batteries, electronic, automobile etc. This method can be economically beneficial for undeveloped and developing countries.

## Conclusion

This review communication throws light on the efficiency of snail shell in the treatment of waste water. The observations of several research workers illustrate reduction of many physico-chemical parameters such as nitrates, phosphates, sulphates, total solid, turbidity conductivity, COD, BOD and an increase in DO, thus improving the water quality.

Various heavy metals such as cadmium, lead, nickel, cobalt, arsenic, mercury etc. which are most commonly found in industrial waste could also be removed using mollusc shell dust treatment. Thus, it can be a sustainable way for waste water treatment in future.

## References

Adoni, A. D. 1985. *Workbook on Limnology*. Pratibha Publ. Sagar. India

Ahalya, N., Ramachandra, T. V. and Kanamadi, R. D. 2003. Biosorption of Heavy Metals. *Res.J.Chem. Environ.* 7(4) : 01-08.

Alissa, E. M. and Ferns, G. A. 2011. Heavy metal poisoning and cardiovascular disease. *J. Toxicol.* 01-21.

Al-Daamy, M. A., AL-Shemary, R. Q. and Kareem, E. T. 2018. Study on the use of snail shell as adsorbrnt for removal of Azure A dye from aqueous solution. *J. Int. Pharm. Res.* 45 : 123-129.

Al-Saeedi, J. Y., Akbar, M. M. and Al-Qarooni, H. I. 2019.

Removal of Pb (II) and Ni (II) Ions from aqueous solution by Sea Snail Shells. *J. Bio. & Env. Sci.* 14(3) : 17-23.

APHA. 1998. *Standard Methods for the Examination of Water and Wastewater.* 20th edition. APHA-AWWA-WEF, Washington D. C.New York.

Boro, J., Deka, D. and Thakur, A. J. 2012. A review on solid oxide derived from waste shell as catalyst for biodiesel production. *Renew. Sust. Energ. Rev.* 16(1): 904-910.

Castaneda, M., Mirasol, M. S., Raymundo, L. A. and Solidum J. 2012. Biosorption and Desorption of Lead ($Pb^{2+}$) from Simulated Waste Water Using Freshwater Snail Shells, *Melanoides tuberculata* Muller (Family Thiaridae). *2nd International Conference on Environment and BioScience.* 44 : 54- 59.

Champagne, P. and Li, C. 2009. Use of Sphagnum peat moss and crushed mollusk shell in fixed -bed columns for treatment of synthetic landfill leachate. *J. Mater. Cycles Waste Manag.* 11 : 339-347.

Darmokoesoemo, H., Setianingsih, F. R., Putranto, T. W. L. C. and Kusuma, H. S. 2016. Horn snail (*Telescopium* sp.) and mud crab (*Scylla* sp.) shells powder as low cost adsorbents for removal of $Cu^{2+}$ from synthetic wastewater. *Rasayan J. Chem.* 9(4): 550-555.

Das, N., Vimala, R. and Karthika, P. 2008. Biosorption of heavy metal -An overview. *Indian J. Biotechnol.* 7 : 159-169.

Gadd, G. M. 2009. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J. Chem. Technol. Biotechnol.* 84 (1) : 13-28.

Hossain, A. and Aditya, G. 2013. Cadmium biosorption of shell dust of the fresh water invasive snail *Physaacuta*. *J. Environ. Chem. Eng.* 1(3) : 574-580.

Ikhuoria, E. U. and Uyammadu, C. U. 2001. Adsorption of heavy metals on modified snail (*Archachatina marginata*) shell. *Ghana J. Sci.* 41: 29-33.

Jatto, E. O., Asia, I. O., Egbon, E. E., Otutu, J. O., Chukwuedo, M. E. and Ewansiha, C. J. 2010. Treatment of Waste Water from Industry Using Snail Shell. *Academ Arena.* 2(1) : 32-36.

Jung, J. H., Yoo, K. S., Kim, H. G., Lee, H. Y. and Shon, B. H. 2007. Reuse of waste oyster shells as a $SO_2/NO_X$ removal absorbent. *J Ind Eng Chem.* 13(4) : 512-517.

Kaplan, D. L. 1998. Mollusc shell structure: novel design strategies for synthetic material.*Curr Opin Solid State Mater Sci.* 3(3) : 232-236.

Kwon, H. B., Lee, C. W., Jun, B. S., Yun, J. D.,Weon, S. Y. and Koopman, B. 2004. Recycling waste oyster shell for eutrophication control. *Resour Conserv Recy.* 41(1): 75-82.

Liu, Y., Sun, C., Xu, J. and Li, Y. 2009. The use of raw and acid-pretreated bivalve mollusk shell to remove metal from aqueous solutions. *J. Hazard. Mater.* 168(1) : 156-162.

Mathew, B. B., Jaishankar, M., Biju, V. G. and Beeregowda, K. N. 2016. Role of bioadsorbent in reducing toxic metals. *J. Toxicol.* 2016 : 01-13.

Naik, S., Megha., Aishwarya, J. and Shwetha. 2016. Waste water treatment using shell of marine source. *Res J. Chem. Environ. Sci*. 4(4S) : 123-128.

Shahzad, S., Shahzad, N., Yaqub, A., Sadiq, U., Ahmad, U., and Hussain, M. 2017. Removal of heavy metal lead (Pb)(a!) by biosorption process using paper shell mussel (*Anoddontoides ferussacianus*). *WJPMR*. 3(6) : 281-288.

Udeozar, S. O. and Evbuomwan, B. O. 2014. The Effectiveness of Snail Shell as Adsorbent For Treatment of Waste Water From Beverage Industries Using $H_3PO_4$ As Activating Agent. *IOSR-JEN.* 4(1) : 37-41.

Volesky, B. and Holan, Z. R. 1995. Biosorption of Heavy Metals. *Biotechnol. Prog.* 11(3) : 235-250.

Wang, J. and Chen, C. 2016. Biosorption of heavy metals by *Saccharomyces cervecies*: a review. *Biotechnol. Adv.* 24(5) : 427-451.

Weerasooriyagedra, M. S. and Kumar, S. A. 2018. A review of utilization of Molluscan shell for the removal of contaminants in industrial waste water. *IJSRP*. 8(1): 282-287.

WHO. 1993.Guidelines for Drinking Water Quality, Volume '!, a!, b!. World Health Organization, Geneva.

Xu, X., Liu, X., Oh, M. and Park, J. 2019. Oyster Shell as a Low-Cost Adsorbent for Removing Heavy Metal Ions from Wastewater. *Pol J Environ Stud.* 28(4): 2949-2959.