Journal of Engineering Science 13(1), 2022, 73 - 79
DOI: https://doi.org/10.3329/jes.v13i1.60564

JES
an international Journal

HYBRID TREATMENT OF TANNERY EFFLEUENT BY NATURAL COAGULANTS FOR VEGETATIVE SEED GERMINATION

Md. Abdulla-Al-Mamun*[1] and Quazi Farjana Lamia[2]

[1] *Institute of Leather Engineering and Technology, University of Dhaka, 44-50 Hazaribagh, Dhaka-1209 Bangladesh*

[2] *Department of Leather Engineering, Faculty of Mechanical Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh*

Received: 27 December 2021 Accepted: 04 June 2022

ABSTRACT

Treatment of the tannery wastewater by mixing the effluents in desired ratio, with natural coagulants prepared by using natural elements and small quantity of chemicals is a cost-effective method. Here, indigenous natural-coagulant named chitosan extracted from shrimp-shell and Morinaga Oleifera seed as a bio-absorbent was used. To the best of knowledge, this comprehensive hybrid method not been investigated yet for tannery effluent treatment. Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. The Chitosan and Morinaga seeds extraction works on wastewater treatment in an excellent way. The reduction of BOD, COD, Salinity proves the effectively of these prepared coagulants from natural elements. Resultant coagulant treated wastewater significantly reduced the pollutants were 97% TDS, 46% COD, 10% Salinity and 43% BOD respectively and removal proves the effectivity of these prepared coagulants. Moreover, it will help on the designing a low-cost chemical free treatment technology of the tannery effluent as for attracting the tannery-owner to set up a treatment plant. At the same time, the effect of the treated water to the vegetative seed germination and growth was also examined. That can be identified the impact of application of the treated wastewater for irrigation.

Keywords: *Coagulants; Chitosan; Moringa Oleifera; Tannery Effluent.*

1. INTRODUCTION

Leather manufacture process involves a huge number of chemicals and mechanical operations are needed in leather tanning process. The tanning process consists of four major groups and other sub-processes required to making finished leather. The major groups are called the beam house operation, tan yard, retanning and finishing processes which is summarized in a unit leather processing (Lofrano; Meric; Balci and Orhon, 2003). The first sub-process is soaking, liming, unhairing, fleshing, splitting, bating, degreasing and pickling. It is reported that only 15 % of offered chemicals are retained in the finished leather, while the residue of 85 % chemicals enters the waste streams was determined by UNIDO (UNIDO, 2000).

The generated solid and liquid wastes are mostly discharged without treatment from the tanneries is the main reason to pollute the adjacent river and localized eco-system (Azom; Mahmud; Yahya; Sontu and Himon, 2012). On an average of 30–35 m^3 of wastewater is produced per ton of raw hide (Tunay; Kabdaşlı; Orhon and Genceli, 1995). Mainly pollutants of blood, manure, soluble proteins, emulsifying agents, sulphides, high alkalinity, suspended solids (hairs and lime) proteins nitrogenous matter, high COD and BOD, ammonium salts, inorganic acids, fats, degreasing agents, chromium III salts, sulphate and carbonates are generated from beam house and tanning processes (Abdulla-Al-Mamun; Goush, 2019). The impact of tannery effluent includes the presence of ammonia and nitrates in water is toxic to organisms, if the quantities greater than 10 mg/l. The sulphide constituent of effluent is significant as hydrogen sulphide, which is a highly toxic gas (Money, 2003). The absence of oxygen promotes the anaerobic putrefactive fermentation, especially in the presence of protein resulting in foul odors. Bangladesh earns significant amount of foreign currency by exporting leather goods from its tanning industries. A recent report revealed that leather and leather products are one of the major external trade sectors which contribute up to 1.39% share on the total export earnings (EPB, 2010). But the tannery effluent is polluting the water bodies and creating a huge environmental pollution and treatment of tannery wastewater is always required.

*Corresponding Author: *mamun.ilet@du.ac.bd*

Various physico-chemical techniques have been studied for their applicability to the treatment of tannery wastewater. These are coagulation and flocculation, reverse osmosis, ion exchange, adsorption, activated sludge process, membrane processes, advanced oxidation processes, photo oxidation processes, electrochemical treatment etc. (Tunay et al., 1995). Among all, the chemical-based treatment methods, created the chemical containing sludge, which is a great problem for the treated effluent. However, above stated methods required high cost for plant set up, but we all known that waste treatment is an economically mostly zero output method. So, the industrialists are not interested to set up a high-cost plant for wastewater treatment.

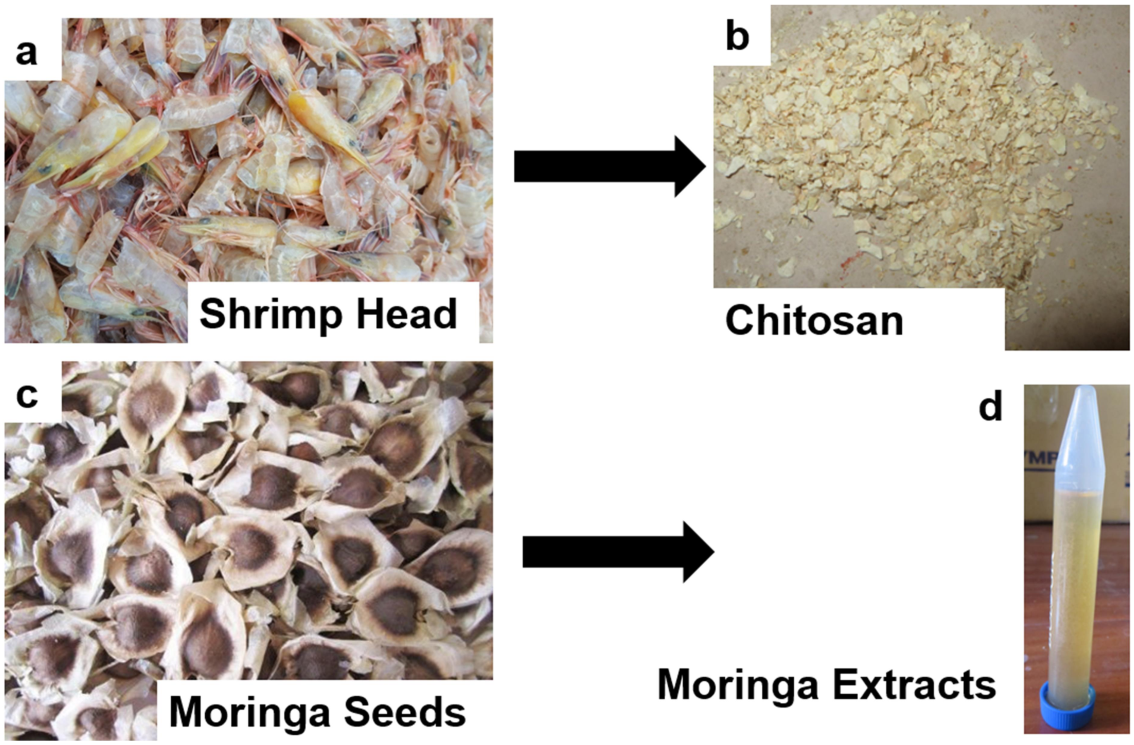

Figure 1: Picture of Shrimps shell and Morinaga Oleifera (Sajna) seed. (a) Shrimps shell (b) Chitosan (c) Morinaga seeds (d) Morinaga Oleifera extract.

Chitosan has several commercial and possible biomedical uses. In our country, especially Khulna region have a lot of shrimps' sources due to the salty coastal area. This region is famous for the shrimps exporting and easily found shrimps shell as a byproduct. On Figure 1, the pictures of shrimps shell, Moringa oleifera (Sajina) and their extract conversion process which is covers the highest utilizations of byproduct.

Chitosan can also be used in water processing engineering as a part of a filtration process. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. It also removes phosphorus, heavy minerals, and oils from the water. Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity (Woodmansey, 2006). Side by side Moringa Oleifera which is an effective natural coagulant for wastewater treatment. Moringa oleifera (MO) is a multipurpose tree with considerable potential and its cultivation is currently being actively promoted in many developing countries. Seeds of this tropical tree contain water soluble, positively charged proteins that act as an effective coagulant for water and wastewater treatment (Shan et al., 2017). Most of the water treatment process and chemicals are very costly and Moringa oleifera could be an alternative to it (Lea M., 2010). In this experiment the effectivity of Chitosan, Moringa Oleifera and dual action of them has been analyzed by optimization of dosage, time, and pH. The characterization of treated wastewater has been done in terms of Turbidity, pH, BOD, COD, Salinity and Conductivity (Sabur et al., 2013).

In this paper, we introduced the new kinds of locally available byproduct based natural coagulant and established the new kinds of effluent treatment with a good efficiency.

2. EXPERIMETAL

2.1 Materials and method

Tan yard effluent such as soaking, liming, deliming and pickling were collected from a tannery (SAF tannery, Jessore) and primarily filtered by glass wool. The filtered effluent was preserved in freeze at 4 °C. The tan yard soaking and liming effluent have the protein, hair, different kinds of salts and emulsified fats which are increased the contents of TDS, BOD, COD, and Salinity etc. Deliming and bating effluent contain sulphides, ammonium salts, calcium salts, and the effluent is slightly alkaline. The pickling effluents contain minarel acid, chlorides, and the effluent is slightly acidic.

The Shrimps shell, Morinaga oleifera (Sajina), and Bottle gourd seeds used in this study were obtained from nearby the KUET campus and local market of Khulna city, respectively. The shells were washed, air dried and sun dried for four consecutive days at normal atmospheric temperature. The dried shell was packaged in air-tight plastic zipper packet and preserved for next operation to extraction chitosan.

2.2 Preparation of synthetic mixing effluent

Mixing the effluents of soaking, liming, deliming and pickling at ratio of 7: 4: 1.75: 0.75 respectively to get optimum settlement as reported in UNIDO 2003 for beamhouse pollution load of tannery effluent (Bosnic et al., 2003). The calculation was done to total of all ratios as 13.5 and the value converted to liter to following the law (Ratio gradient/13.5 x1000) ml. The process was optimized by measuring settled solids using Imhoff sedimentation cone. The supernatant from the Imhoff cone was characterized and used for the next operation.

2.3 Extraction of Chitosan and Moringa Oleifera (Sajina)

Chitosan was prepared using a combination of three procedures reported in elsewhere (Okuda et al., 1999). Five gram of shrimp shell waste was treated with 4% NaOH at room temperature for 24hours. The alkali was drained from the shells and washed with distilled water repeatedly till pH dropped to neutral. This process caused deproteinization of shells. The deproteinized shells were treated with 4% HCl at room temperature for 12hours for demineralization to yield chitin. The acid was drained off from chitin, washed with distilled water and finally dried at room temperature. The process was repeated with 2% NaOH and 1% HCl. The chitin obtained still had a slight pink hue. Further decolorization was achieved by soaking chitin in 1% potassium permanganate for 30 mins followed by 1% oxalic acid for 30 mins to 2hours. The decolorized chitin was deacetylated to form chitosan by treating with 65% NaOH for 3 days at room temperature. Alkali was drained off and washed repeatedly with distilled water till pH was lowered. Chitosan was further dried at room temperature and stored.

To prepare coagulant from Moringa Oleifera, Mature seeds were allowed to dry, and the shell of seeds were removed. The seed kernels were ground to fine powder using a kitchen blender to make it of approximate size of 600 µm to achieve solubilization of active ingredients in the seed. Powder of Cicer arietinum (commercial name bashion) was bought from local market of khulna city. The grains of powder were maintained approximate size less than 600 µm to achieve solubilization of active ingredients in the seed. Mature seeds of Dolichos lab were used in the study. After sun dry, external shells were removed and seed kernel were obtained. Distilled water was added to the powder to make 1% suspension of it. The suspension was vigorously shaken for 45 minutes using a magnetic stirrer to promote water extraction of the coagulant proteins, and this was then passed through filter paper (Whatman no. 42, 125mmdia.). The filtrate portions were used for required dose of natural coagulants. Fresh solutions were prepared daily and kept refrigerated to prevent any ageing effects (such as change in pH, viscosity, and coagulation activity).

2.4 Characterization of Treated and Untreated Water for Seeds (Bottle gourd) Germination

Turbidity is one of the important aesthetic properties of potable water, and it is also very useful in defining drinking water quality. Turbidity was measured using turbidity meter (Model-2100 Q, HACH, USA). The pH of water was measured by using a pH meter (EZODO, Model- PH 5011, USA). Conductivity, TDS and salinity was measured by portable meter (Model-CT 676, BOECO, Germany). The performance of coagulants were analyzed on the basis measurement of BOD, COD and TDS. The BOD and COD method was followed by the EPA-600/4-7-20 USEPA, Method 405.1 and Method 410.1, respectively. After treatment of the seed germination experiment was carried out. The soil full on two plastic jar and 2 (two) seeds of bottle gourd were placed on a soil containing each plastic jar. The jar was then placed on Leather Engineering Department lobby, KUET, Bagladesh. The same amount (ca. 200 ml) of treated and untreated tannery effluent was then poured on surface of soil at daily basis and germination counts were taken daily for 16 days.

3. RESULTS AND DISCUSSION

Several parameters have been selected here to characterize the quality of treated water. As turbidity is one of the most important properties. It has been selected to determine the optimum time, dosage of coagulants and pH. The turbidity was measured 120, 150, 180, 210, 240 min-time interval with different dosage of coagulant at different pH. Figure 2 demonstrates, the optimization of coagulant dosage and time. As the turbidity is lowest at 180min, so this has been considered as optimum treatment time (Fig 2). The optimum dosage of chitosan is 0.125gm/50ml (Fig 2A (a)) and for moringa the dosage is 1.5ml/50ml (Fig 2B(c)) respectively.

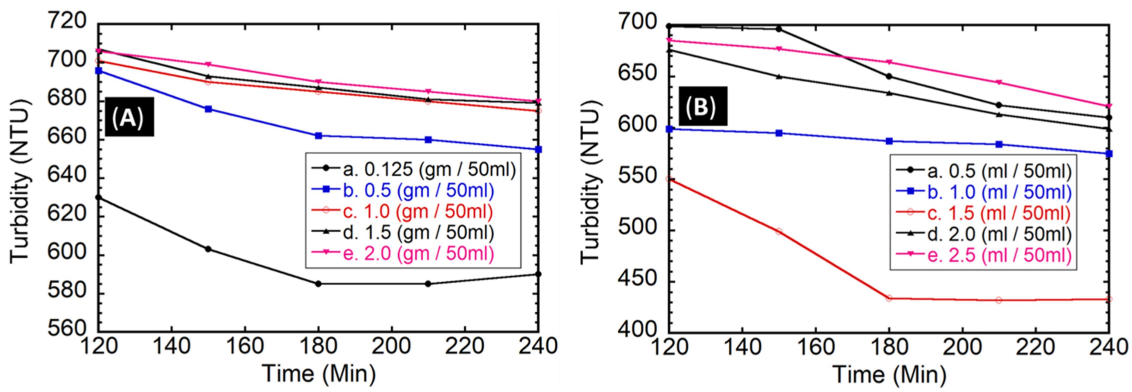

Figure 2: (A) Optimum dosage of Chitosan and (B) Optimum dosage of Moringa.

The dosage for removal of turbidity depends on the bridging between the pollutants and active site of the coagulants. With 0.125gm chitosan, shows the highest degree of turbidity removal which is 41%, because bridging of pollutants and chitosan active sites were highest with this amount. Chitosan was added as flakes for this reason lower amount of chitosan gave an effective turbidity removal with the appropriate bridging. For moringa, it was added as liquid and too lower amount of moringa has lower active sites, but the turbidity removal rate increases with the increase of dosage. The optimum removal turbidity was found 56% with a doses of 1.5 ml Moringa Oleifera. This is because the sample volume remained same but increased moringa concentration was providing more active sites. Too lower amount of chitosan/moringa cannot provide enough active sites for pollutants and higher amount increases the solid content of liquid itself.

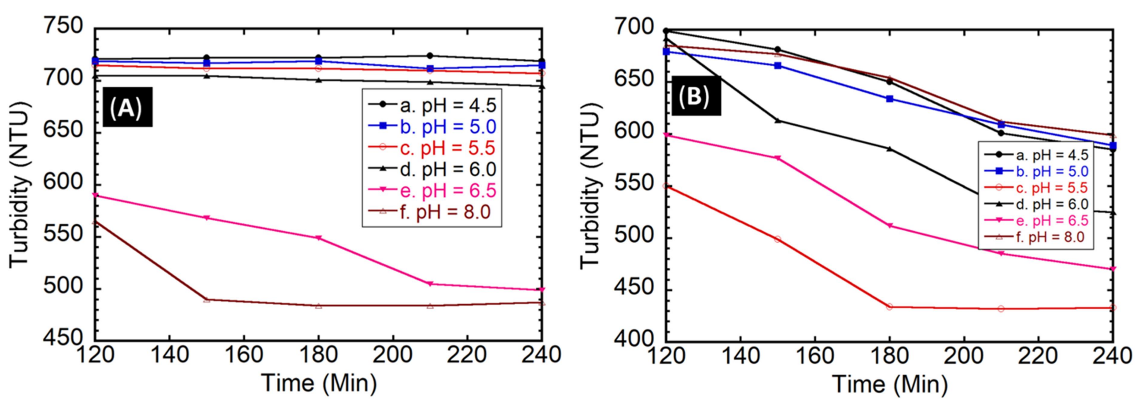

Figure 3: (A) Optimization of pH with Chitosan and (B) Optimization of pH with Moringa.

The highest turbidity removal for chitosan is at pH 8 (Fig 3(A) (f)) because the chitosan is soluble in an aqueous solution which has pH greater than 6, but not too much acidic. For moringa, the best working pH is 5.5 (Fig 3(B) (c). However, the chitosan and moringa needs two different pH range. The adjustment of pH to the acidic range was done by adding 1M HCl and to alkaline pH 1N NaOH. The acid and alkali was added drop by drop with a stirring device for proper mixing.

After the single treatment with chitosan and moringa the dual action has been tested and the optimum pH has been found 8.5 (Fig 4(g)) where the turbidity removal is highest. Chitosan and Moringa has two different pH range while they work together the best treatment came out at alkaline pH range.

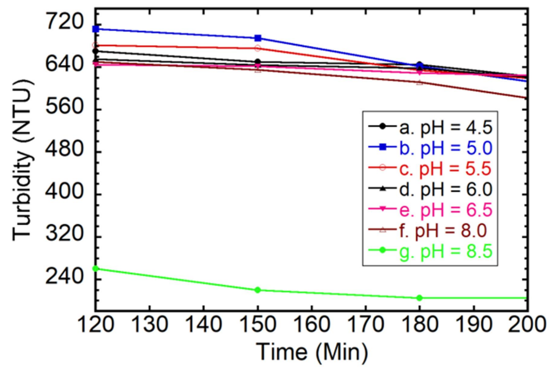

Figure 4: Optimization of pH with optimum amount of Chitosan and Morinaga dual treated wastewater.

Chitosan is easily soluble to acidic solution and moringa is highly alkaline and when they are added together the pH of the liquid increases. Alkaline pH accelerates the precipitation of pollutants and at 8.5 pH the removal of turbidity was highest because the pH range 8-8.5 is an ideal pH range for most of the coagulants and moringa-chitosan is one of them (Vigneshwaran et al., 2020). The amount of the wastewater for this measurement of coagulants are 50ml which has been calculated by several trial-and-error experiments. At pH 8.5 and 0.125gm of chitosan with 1.5ml moringa within 180 min showed the best treatment result. The results from only Chitosan is good because it requires in very small amount (0.125gm) compared to Morinaga. But when Chitosan and Morinaga used together the result was excellent because the turbidity is 202 NTU and removal efficiency is ca. 97%.

Table 1: Effect of Chitosan, Moringa and Dual (Chitosan and Moringa) on Conductivity, Salinity, BOD, COD and TDS of wastewater.

Name of the reagent	Conductivity		TDS		Salinity		BOD		COD	
	Untreated mS	Treated mS	Untreated gm/ L	Treated gm/L	Untreated ppt	Treated ppt	Untreated mg/L	Treated mg/L	Untreated mg/L	Treated mg/L
Chitosan	36.7	36.1	17800	10000	23	22.8	2100	1600	35000	25000
Moringa	36.7	34.58	17800	8900	23	21.9	2100	1500	35000	27000
Dual (Chitosan & Moringa)	36.7	33.58	17800	628	23	20.8	2100	1200	35000	19000

Wastewater treated with Chitosan and Morinaga extract showed a huge reduction of BOD, COD, and Salinity shows in Table 1. Dual action is best for effluent treatment rather than Morinaga seed extract or Chitosan singly. The BOD of treated water reduced to 1200 mg/L from 2100 mg/L and the COD decreased to 19000 mg/L from 35000 mg/L. Other parameters Conductivity, Salinity and TDS have been decreased to 33.58 mS/cm, 20.8ppt and 628 mg/L respectively under the dual action of chitosan and moringa oleifera. The TDS removal efficiency is ca. 97%. After 180 min of treatment the final pH of the treated effluent was 8. However, Chitosan and Moringa has two different pH range while they work together the best treatment came out at alkaline pH range. This is because, the alkalinity of the water provides proper hydroxyl ion to the solution. The coagulants make an intermediate aqua coagulants ions. If, the pH is in alkaline range the availability of the hydroxyl ions in the solution makes coagulation process effectively.

After the treatment of wastewater with chitosan and moringa germination has been carried out to make a comparison of quality of treated water. Another important physical property is colour which was black before treatment and colourless after treatment.

3.1 Test of seed Germination

Resultant treated water obtained (Fig 5) in this study showed that seeds grown with untreated water is preventing the growth. The growth of the plant within three days is only about 1.5 cm shown in Figure 5(a). Similar in treated water growth is not hamper at all and found more than 3 cm shown in Figure 5(b). The observed results of final germination pooled together were contrary to the expectation that chitosan and morinaga dual treated water should perform better than untreated effluent. In case of seed germination, it is very clear from the figure that the growth of seed with treated water is more than the untreated water as well as the health of the plant is better in treated water.

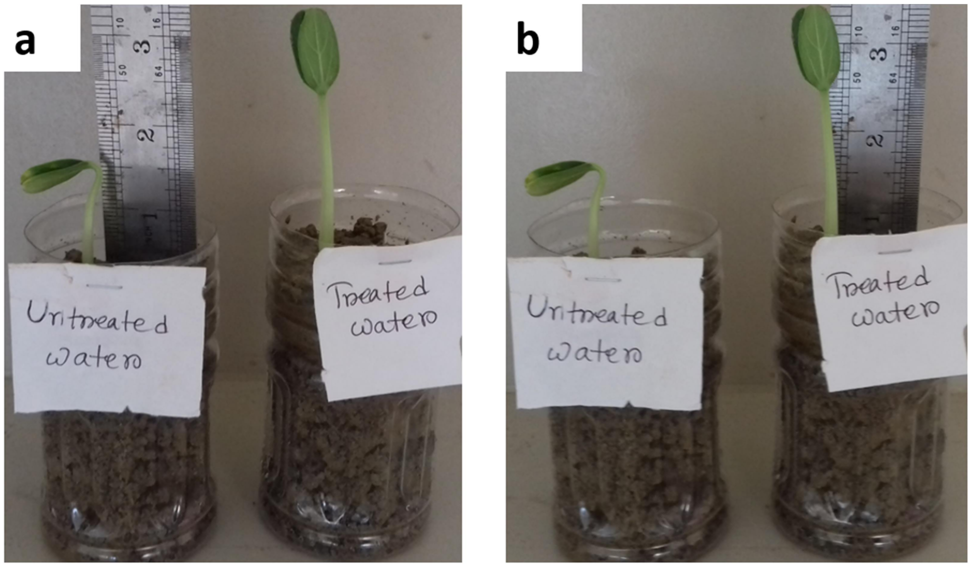

Figure 5: Optimum Chitosan and Moringa dual treated, low turbid effluent and untreated raw effluent for tested the seed germination. (a) Untreated water seed germination with scale (b) Chitosan and Moringa dual treated low turbid water.

4. CONCLUSIONS

Based on research results, it can be concluded that the indigenous natural-coagulant chitosan extracted from shrimp-shell and from Morinaga seeds has good prospect to use for tannery yard effluent treatment by means of low-cost effluent treatment. The treated effluent can easily be used for the vegetable plantation. This is the primary finding for effectiveness of coagulants on tannery yard effluent. The overall treatment takes a little bit longer time than the conventional chemical coagulants but the ultimate effectiveness for pollution removal from wastewater specially the turbidity, BOD, COD, salinity and germination quality of seed is better. After completing the treatment, germination of seeds was also analyzed with the treated and untreated water. The germination rate was higher and the growth rate of the plant from seed with treated water. When Chitosan and Moringa Oleifera works together it could be a best alternative to other chemical coagulants. Though the Moringa Oleifera could grow some pathogens if it stays in the bottom of the treatment chamber for a long time, but it could be easily removed in secondary treatment of by disinfecting the chamber. Treated water also shows the result that falls under the permissible limit. Based on research results, Chitosan and Moringa Oleifera treated water can easily be used for seed germination or can be discharged into nearby water bodies or into the secondary treatment chamber for biological treatment.

ACKNOWLEDGEMENT

This research was partly supported by the University Grant Commission, Bangladesh (No. KUET/CASR/16/55(25), Date: 28/08/2016). The authors greatly acknowledge to Khulna University of Engineering & Technology, Bangladesh for their UGC funded Grant-in-Aid for this research project.

REFERENCES

Abdulla-Al-Mamun M., Goush B.R., 2019. Potential of Functionalized-Rice-Husk Ash for Purification of Tannery-yard Liming Effluent. J. Sci. Res. 11 (3), 373-381.

Azom M. R., Mahmud K., Yahya S. M., Sontu, A., Himon S. B., 2012. Environmental Impact Assessment of Tanneries: A Case Study of Hazaribag in Bangladesh. *Int. J. Environ. Sci. Dev.* 3(2), 152–156.

Bosnic M., Buljan J., Daniels R. P., Rajamani S., 2003. Pollutants in tannery effluent: International Scenario on Environmental Regulations and Compliance, Vienna: United Nations Industrial Development Organization (Unido), pp. 11-14.

Bouchareb R., Derbal K., Benalia A., 2021. Optimization of active coagulant agent extraction method from Moringa Oleifera seeds for municipal wastewater treatment. *Water. Sci. Technol.*, *84*(2), 393–403.

Export Promotion Bureau, Ministry of Commerce,"2009-2010 Annual Report", Dhaka: The Peoples Republic of Bangladesh, Chapter 9.

Lea M., 2010. Bioremediation of Turbid Surface Water Using Seed Extract from Moringa oleifera Lam. (Drumstick) Tree. *Curr. Protoc. Microbiol. 16*(1), 1-8.

Lofrano G., Meric S., Zengin G. E., Orhon, D., 2013. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review. *Science of The Total Environment*, *461–462*, 265–281.

Ludvík, J., 2000. Chrome balance in leather processing, Vienna:United Nations Industrial Development Organization (Unido), pp. 1-5.

Money C.A., 2003, 'Utilisation of total dissolved solids by tannery effluent irrigation' *Proceedings of Global Benchmarks for Leather Sector*, CLRI, Chennai, India.

Okuda T., Baes, A. U., Nishijima, W., Okada, M., 1999. Improvement of extraction method of coagulation active components from Moringa oleifera seed. *Water Research*, *33*(15), 3373–3378.

Sabur M. A., Rahman M. M., Safiullah S., 2012. Treatment of Tannery Effluent by Locally Available Commercial Grade Lime. *J. Sci. Res.*, *5*(1), 143–150.

Shan, T. C., Matar M. A., Makky, E. A., Ali, E. N., 2016. The use of Moringa oleifera seed as a natural coagulant for wastewater treatment and heavy metals removal. *Applied Water Science*, *7*(3), 1369–1376.

Tünay O., Kabdasli I., Orhon, D., Ates, E., 1995. Characterization and pollution profile of leather tanning industry in Turkey. *Water. Sci. Technol.*, *32*(12), 1–9.

Vigneshwaran S., Karthikeyan P., Sirajudheen, P., Meenakshi, S., 2020. Optimization of sustainable chitosan/Moringa. oleifera as coagulant aid for the treatment of synthetic turbid water – A systemic study. *Environmental Chemistry and Ecotoxicology*, 2, 132–140.

Woodmansey A., 2006. Chitosan Treatment of Sediment Laden Water - *Washington State I-90 Issaquah Project, Federal Highway Administration. U.S. Department of Transportation*. Retrieved on 2006-07-10