Available Online

**JOURNAL OF SCIENTIFIC RESEARCH**

Publications

J. Sci. Res. **11** (3), 373-381 (2019)

www.banglajol.info/index.php/JSR

# Potential of Functionalized-Rice-Husk Ash for Purification of Tannery-yard Liming Effluent

**M. Abdulla-Al-Mamun*, B. R. Goush**

Institute of Leather Engineering and Technology, University of Dhaka, 44-50 Hazaribagh, Dhaka-1209, Bangladesh

Received 21 March 2019, accepted in final revised form 19 May 2019

**Abstract**

The natural rise-husk charcoal was made by burned in a furnace at 230 °C. Carboxylic group (-COOH) was functionalized onto the charcoal by using oxalic acid in situ process. Fourier Transform Infrared Spectroscopy (FTIR) and morphology by Scanning Electron Microscope (SEM) demonstrated that the COOH-group was successfully functionalized on the charcoal and the particles were porous. The COOH-activated charcoal was applied for liming effluent treatment through a filtration media. Eight environmental load parameters was determined by the standard method. The results were compared with the standard permissible limits set by Inland Surface Water-Bangladesh Standards (ISW–BDS-ECR, 1997). It has been observed that the rice husk based activated carbons dramatically reduce the pollutants to permissible level. The removal efficiency of pH, Electrical Conductivity (EC), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Biological Oxygen Demand in 5 days at 20 °C ($BOD_5$), Chemical Oxygen demand (COD), Total Alkalinity, $S^{2-}$ from liming effluent up to 40.0%, 85.89%, 98.8%, 81.32%, 96.74%, 78.6%, 97.15% and 79.61% respectively. In conclusion, the liming effluent simply recycled by filtration process and can be used for industrial purpose.

*Keywords*: Leather industry; Liming; Effluent treatment; Rice-husk-charcoal; Activated carbon.


doi: http://dx.doi.org/10.3329/jsr.v11i3.40635 J. Sci. Res. **11** (3), 373-381 (2019)

## 1. Introduction

The leather industry is a major industry on an international scale and is of significant economic importance. The industry has received criticism on environmental grounds and the tanning industry has viewed to be a major source of water pollution. The increasing pollution awareness is forces us to seek the environmentally clean alternative pollution mitigation resources like as filtration process. The emergence of functionalized rice-husk-charcoal as the new building blocks to construct filtration assemblies has opened up of new ways to utilize renewable sources. Rice-husk-charcoal have attracted great interest because the unlimited source can be utilized to produce the cost effective and

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

environmental friendly filter. There are many treatment processes including chemical coagulation and flocculation, adsorption, filtration and reverse osmosis etc. [1]. Among these treatment procedures, filtration is considered as the simplest one. In recent years, the application of carbon based nano-material has achieved significant attention due to its large surface area and more active functionalized sites [2-4]. Literature review showed that carbon based materials such as activated carbon, carbon annotates, grapheme oxides are increasingly used in this area [1,5]. In our present study, we made the charcoal based filter to make the cost effective filtration process. Resultant filtered water was measured and a comparative study was done by changing different parameter.

This study proposes the use of rice-husk activated carbon combined with sand and stones of various sizes in different layer for lime liquor treatment. The two principal mechanisms by which activated carbon removes contaminants from water are adsorption and catalytic reduction. Organics have been removed by adsorption and residual disinfectants are removed by catalytic reduction [6]. Carboxylic group of activated carbon prepared from rice husk was used as absorbent and lime liquor have passed through a filtration media, which have been designed and fabricated in laboratory. In addition, the physicochemical parameters was analyzed in comparison with raw liming effluent. In recent years, many researchers approached tannery waste water treatment technology but the liming effluent need to be treated separately as it emits $H_2S$ at lower pH which has adverse impact on the environment as well as human body [1,2]. So far, a group of researcher worked on treating liming effluent by electro-coagulation [7].

Despite many research articles on activated carbon for wastewater treatment, so far there is no publication found devoted to make the liming effluent recycle and reuse by using activated functionalized rice husk. To our knowledge, this is the first time functionalized rice husk-based filtration have been fabricated and successfully used for tanning yard liming-effluent filtrations.

## 2. Experimental

### 2.1. *Collection of rice husk, liming effluent and stone*

Rice husk was collected from Jamalpur district, Bangladesh during July 2018. About, 500 g of rice husk was washed repeatedly through distilled water to remove dirt and other contaminants, oven-dried at 110 °C for 12 h then grounded and sieved to fractions with average particle size of 1.0 mm. The liming wastewater was collected from the Pragati Leather Complex, Savar, Dhaka, Bangladesh during July, 2018. 10 L of liming wastewater was collected in polyethylene container and immediately transported to the laboratory for experimentation. The fine and coarse sand and stone were procured from the construction building plant at Hazaribagh, Dhaka, Bangladesh and thoroughly washed by distilled water at 3-4 times and dried at several days.

**2.2.** ***Chemicals and reagents***

Analytical grade of chemicals and reagents have been used for experimental purposes and further any purification. Oxalic acid ($C_2H_2O_4.2H_2O$), nitric Acid ($HNO_3$), sodium hydroxide (NaOH), sulfuric acid 98% ($H_2SO_4$), hydrochloric acid (HCl), ammonia ($NH_3$), ammonium Chloride ($NH_4Cl$), barium chloride ($BaCl_2$), ferrous sulphate ($FeSO_4$), ethanol ($C_2H_5OH$), potassium dichromate ($K_2Cr_2O_7$; 0.02 mol/L) was purchased from Merck, Germany and ferron solution AR (0.25 M) from Loba Chemie, potassium ferri cyanide ($K_3[Fe(CN)_6)$, dimethylglyoxime ($C_4H_8N_2O_2$) from Uni Chem, India.

**2.3.** ***Preparation of functionalized-rice-husk***

In the first step, dried rise husk were carbonized at 230 °C on hot air oven for 8 hrs. The functionalized rice husk was prepared by the following procedure as shown schematically in Fig. 1. About 100 g of carbonized rice husk was dispersed in 400 mL of distilled water by sonication for 30 min. in a water bath. About 200 mL of oxalic acid was dissolved in 100 mL of distilled water in the presence of a few drops of a 1.0 M aqueous NaOH solution. This alkaline oxalic acid was added to the carbonized rice husk supernatant solution. Then the mixture was stirred for 12 h at 60 °C on a hotplate with a magnetic stirrer (PA 1180, LK LAB Korea). The final product was washed for several times with distilled water until the neutral pH was achieved. The washed COOH-functional-rice-husk sample was dried at 120 °C for 24 h in an oven and stored in a desiccator.

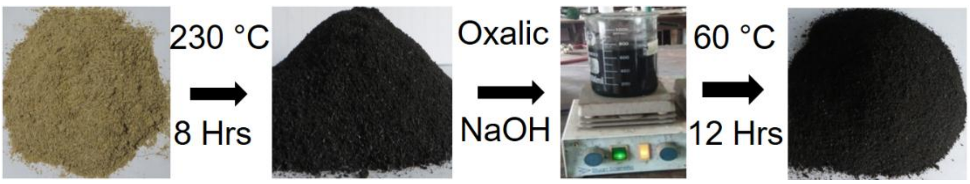


Fig. 1. Schematic flowchart of functional-rice-husk production.

**2.4.** ***Characterizations and measurement of functionalized-rice-husk***

The Scanning Electron Microsscope (SEM, JSM-6490LA, JEOL, Japan) was used for the functionalized-rice-husk imaging and analyzing for surface morphology and structures. The samples were finely powdered (1-2 mg) and dispersed on a conducting carbon glued strip. It was then dried with air by hand pump. The sample loaded strip was mounted to a chamber that evacuated to $10^{-3}$ to $10^{-4}$ torr and then a very thin gold layer was sputtered on the sample to ensure the conductivity of the sample surface. Finally, it was placed in the main chamber of the SEM.

Fourier transform infrared (FT-IR) spectroscopy was performed using an IR Prestige21 spectrometer (Shimadzu Corporation, Kyoto, Japan) over the wave number range of 4000 to 500 $cm^{-1}$. The surface functional groups of rice-husk samples were identified by Fourier transform infrared spectroscopy. In each samples, about 150 mg of dried, KBr was mixed with 1 mg dried sample, grinded homogenously with mortar-pestle and pressed mechanically to make a pellet under the pressure of 8-10 tons. The prepared pellet was placed in the path of IR beam.

Firstly, physicochemical parameters of the untreated wastewater were determined. Secondly, untreated wastewater was filtered through a paper filter (102 qualitative, medium speed, pore 20-30 μm). Eight physio-chemical parameters of the supernatant were determined. Then, the supernatant was filtered through six-layer filter beds, which had a coarse sand layer at the top, functionalized rice husk layer in the middle and fine sand layer at the bottom. These layers was repeated in the same filter for better purification. Width of the filter bed layers were 4 cm for each of the two sand layers and 0.5 cm for the functionalized rice husk one. Finally, the physiochemical parameters of the filtrate were determined.

### *2.5. Analysis method of treated and untreated water*

We characterized to determine the raw liming-effluent and treating filtrated water by the physicochemical parameters analysis. All physical parameters including pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Biological Oxygen Demand in 5 days at 20 °C (BOD5), Chemical Oxygen Demand (COD), and Alkalinity were measured. TDS and TSS were determined by the gravimetrically standard methods of IS-3025 (Part 16 & 17) and alkalinity was determined by the gravimetrically standard methods of IS-3025 (Part 23). A portable pH meter (HANNA instruments) was used to measure the pH. Electrical conductivity (EC) was measured by using the Conductivity Meter (MAKS TRADING LIMITED). Sulfide level was determined by the SLC 202 official methods (Society of Leather Technologist and Chemists, 1996). The analysis results were compared with the standard permissible limit (The Environment Conservation Rules, 1997) for wastewater discharge to evaluate the filter efficacy.

## 3. Results and Discussion

### 3.1. *SEM image and FTIR spectra analysis*

Scanning electron micrographs of functionalized rice husk (a) before and (b) after filtration of the liming effluent are shown in Fig. 2. It can be seen from the pictures that all the functional rice husk samples exist aggregated together to form pieces with different sizes. The size of the pieces increases lightly after filtration of liming water. This change in particle shape has signifies the adsorption of liming effluent. All the samples have rough and porous structure with cracks and crevices. Fig.2(c) shows the high-magnified SEM images and (d) shows the corresponding insert figure. Insert figure clearly revealed that, the functionalized rice husk have porosity.

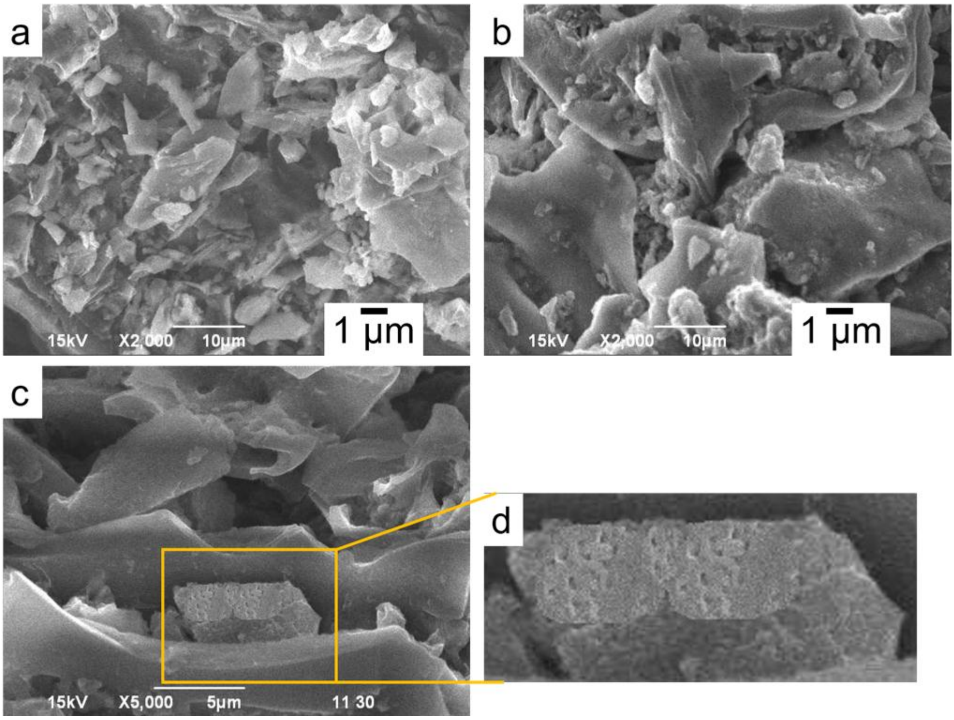


Fig. 2. SEM images of (a) Functionalized rice husk at before lime effluent treatment (b) Functionalized rice husk at after lime effluent treatment. The scale bar has shown 1 µm. (c) shows the high magnification functionalized rice husk and (d) Insert shows the porosity of functionalized rice husk.

The FTIR spectra was studied to measure wavelength and intensity which have characteristics of specific types of molecular vibration and stretching that help to identify functional groups of sample in surface as shown in Fig.3. The formation of new bands confirms the presence of binding of -COOH to the carbonized rice husk on the surface.

The FTIR spectra were recorded in the spectral region of 4000–500 $cm^{-1}$ and their frequency assignment was discussed. The FTIR spectra of carbonized rice husk show high absorption broad peaks at 3423 $cm^{-1}$, indicating the presence of –OH groups on the surface of rice husk during the functionalized of charcoal. The highly intense peak of carbonized and functionalized rice husk at 1576 $cm^{-1}$ can be ascribed to the C=C skeletal vibration of charcoal carbon. In addition, the spectra band from 1070 $cm^{-1}$ can be ascribed to the presence of oxygen moieties, C=O carbonyl groups. Peak at 2921, 2849 and 700 $cm^{-1}$ have confirmed the presence of C-H (alkanes) groups in carbonized and functionalized rice husk. Furthermore, a prominent new peak appeared in the functionalized rice husk charcoal at 1730 and 1373 $cm^{-1}$ due to the -COOH groups on the surface. Therefore, FTIR confirmed the presence of the -COOH groups modifier on the surface of the carbonized rice husk.

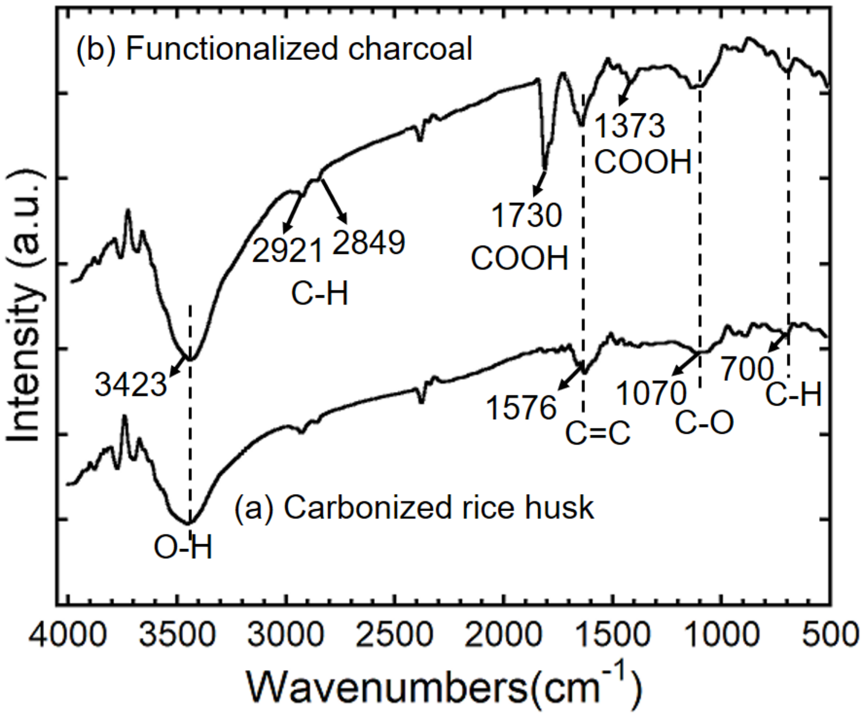

Fig. 3. FTIR spectra of (a) carbonized (non-functionalized) rice husk and (b) functionalized carbonized rice husk after 10000 cycles.

### 3.2. *Treatment of liming-effluent and performance analysis*

The analysis results of untreated (raw) and treated effluent are presented in Table 1. The results were done by five times and average was shown in Table.1. Results signifies that the liming effluent had strong pollution loads and contained higher quantities of pollutants. As liming wastewater is highly threatening to the environment, it is very important to treat the liming wastewater properly to reduce its polluting potency.

The pH of the collected liming effluent (untreated) and purified water (treated) was measured by a portable pH meter. The pH values of untreated liming effluent were observed 12.0±0.5, which is higher than the permissible limit pH 6-7. After treating the effluent by using functionalized rice husk through the filtration media, the result found was 7.5±1.0, which is in the permissible range.

Electrical Conductivity (EC) values at 25 °C of untreated liming effluent were observed 34.02±0.4 mS/cm that is approximately 32.5 higher than the permissible limit (ECR, 1997). After treating the effluent by using functionalized rice husk in a filtration media, the result was found 4.8±0.45 mS/cm.

The average total suspended solid (TSS) values of untreated liming effluent were observed 16348±250 mg/L, which is very high, compared to the permissible limit (ECR, 1997). After treating the effluent by using functionalized rice husk charcoal in a filtration media, the result found was 450±150 mg/L, which is very close to the permissible range.

Table 1. Removal of pollution load from liming wastewater (optimized condition) and comparison with the standard permissible limit (The Environment Conservation Rules, 1997).

| Parameter | Unit | Limning effluent | After filtration | Standard permissible limit, ECR 1997 [8] | | |
|---|---|---|---|---|---|---|
| | | | | Inland | Irrigation | Tannery |
| pH | - | 12.0±0.5 | 7.5±1.0 | 6-9 | 6-9 | 6-9 |
| Electrical conductivity | mS/cm | 34.02±0.4 | 4.8±0.45 | 1.2 | 1.2 | 1.2 |
| TSS | mg/L | 16348±250 | 450±150 | 150 | 200 | 100 |
| TDS | mg/L | 21206±165 | 3959.5±230 | 2100 | 2100 | 2100 |
| $BOD_5$ | mg/L | 4605±500 | 150±50 | 50 | 100 | 100 |
| COD | mg/L | 10080±500 | 2140±400 | 200 | 400 | - |
| $S^{2-}$ | mg/L | 39±0.2 | 1.11±0.1 | 1 | 2 | - |
| Total alkalinity | mg/L | 12115±62 | 2470±250 | - | - | - |

The total dissolved solid (TDS) values of untreated liming effluent was observed at 21206±165 mg/L that is very high compared to the permissible limit (ECR, 1997). After treating the effluent by using functionalized rice husk in a filtration media, the result found was 3959.5±230 mg/L, which is still very higher than the permissible range. Still, working is going on to minimize the TDS in our filtration system.

The average $BOD_5$ values of untreated liming effluent were observed 4605±500 mg/L which is very high compared to the permissible limit for (The Environment Conservation Rules, 1997). The result is very unfair for aquatic lives. After treating the effluent by using functionalized rice husk in a filtration media, the result was found 150±50 mg/L which is in the permissible range.

The average COD values of untreated liming effluent were observed 10080±500 mg/L, which is very high, compared to the permissible limit (ECR, 1997). The results is very unfair for aquatic lives. After treating the effluent by using functionalized rice husk in a filtration media, the result found was 2140±400 mg/L, which is still far from the permissible range.

The average values for total alkalinity of untreated liming effluent were observed 12115±62 mg/L, which is very high, compared to the permissible limit for (ECR, 1997). The result is very unfair for aquatic lives. After treating the effluent by using functionalized rice husk in a filtration media, the result found was 2470±250 mg/L, which is still far from the permissible range.

The average values for Sulfide of untreated liming effluent were observed 39±0.2 mg/L, which is very high, compared to the permissible limit (ECR, 1997). The result is very unfair for aquatic lives. After treating the effluent by using functionalized rice husk in a filtration media, the result found was 1.17±0.1 mg/L, which is very close of the permissible range.

All parameters are acceptable level, except COD and total alkalinity. We are working to improve our filtration system to minimize the both of this two. However, our target to recycle the liming effluent to use further in liming process as to reduce the sulphur content. We successfully had done this and about 98% removed by our filtration process. Our treated water have been underway using in liming process and will be presented in our full paper.

### 3.3. *Removal efficiency of the treatment process*

The removal efficiency of the treatment process have been presented in Table 2. The percentage of removal of EC, TSS, TDS, BOD5, COD, sulfide and total alkalinity were found 85.89%, 98.8%, 81.32%, 96.74%, 78.6%, 97.15% and 79.61% respectively. The efficiency was calculated by following law:

$$(\%) \text{ of efficiency} = 100 - \frac{\text{After filtration} * 100}{Initial}$$

Table 2. Removal Efficiency of pollution load from liming wastewater.

| Parameter | Unit | Initial | After Filtration | Removal (%) |
|---|---|---|---|---|
| pH | - | 12.0±0.5 | 7.5±1.0 | 40.0* |
| Electrical conductivity | mS/cm | 34.02±0.4 | 4.8±0.45 | 85.89 |
| TSS | mg/L | 16348±250 | 450±150 | 98.8 |
| TDS | mg/L | 21206±165 | 3959.5±230 | 81.32 |
| BOD5 | mg/L | 4605±500 | 150±50 | 96.74 |
| COD | mg/L | 10080±500 | 2140±400 | 78.6 |
| $S^{2-}$ | mg/L | 39±0.2 | 1.11±0.1 | 97.15 |
| Total alkalinity | mg/L | 12115±62 | 2470±250 | 79.61 |

*Adjusted pH

The results of the present study illustrated that the functionalized rice husk charcoal has showed maximum pollutants removal capacity from the tannery yard liming effluent. This method is very simple and cost effective as well inexpensive, also materials is an indigenous sources. However, other filtration method have used huge amount of chemicals compare to the present study. It may be suggested that low cost functionalized rice husk could reduce the sulphur and reduce the environmental burden by recycle and reuse of liming effluent. Therefore, this treatment process could be an efficient, cost-effective and eco-friendly process for the removal of pollutants from leather industries lime yard effluents. Analysis of the flow rate of effluent flowing through the functionalized rise-husk charcoal filtration system was step that was necessary. We made the prototype treatment system and will be analyzed with let the effluent flow through the functionalized rise-husk filtration model, and then measured the volume of wastewater at the inlet and outlet.

## 4. Conclusion

This experiment determined the physical and chemical properties of wastewater both inflow and outflow from the filtration system. This study also evaluated the efficiency of wastewater treatment with a systemic way. The parameters such as pH, EC, TSS, TDS, $BOD_5$, COD, sulfide and total alkalinity showed that the untreated tannery-yard lime effluents contained extremely high values of pollutants. These values were far above the standard prescribed limits ECR, 1997. However, environmental regulations and laws in state have been passed rapidly during the last decade. But the compliance has not always been practical, because we have lack of effective instrumental and institutional support. For this region, we fabricated a simple filtration system by using activated rice-husk charcoal with indigenous sources and low cost. Our study illustrate that the COOH-functionalized rice-husk filtration process could reduce the certain pollutants level with an efficient way. It was observed that filtration system shows the maximum efficiency and certain removing the major physico-chemical parameters specially sulphur content, which are the standard prescribed limit for ECR, 1997. This study revealed that functionalized rice-husk filtration system could be promising in order to reduce the pollutants from the lime-yard tannery effluent. The purified water could be re-used in all kinds of industrial works except drinking.

## Acknowledgments

This research was partly supported by Grant-in-Aid for National Science and Technology Fellowship 2018-19 (ID. 854) from Ministry of Sci. and Technol., Bangladesh. The present research was also partly supported by the Institute of Leather Engineering and Technology, Dhaka University. The authors would like to thank S. M. Shamsuddin, Director, ILET, Dhaka University for providing insight and expertise that greatly assisted the research. The authors would like to gratefully acknowledge and thanks to Pragati Leather Complex, 55/1 Hazaribagh, Dhaka-1209 for collecting the liming effluent.

## References

1. J. S. George, A. Ramos, H. J. Shipley, J. Environ. Chem. Eng. **3**, 969 (2015). https://doi.org/10.1016/j.jece.2015.03.011
2. H. Y. Li, Bio. Res. **13**, 3135 (2018).
3. B. Ahmmad, Y. Kusumoto, M. Abdulla-Al-Mamun, A. Mihata, and H. Yang, J. Sci. Res. **1**, 430 (2009). https://doi.org/10.3329/jsr.v1i3.2631
4. M. Abdulla-Al-Mamuna, Y. Kusumotob, and G. J. Islamc, J. Sci. Res. **5**, 245 (2013). https://doi.org/10.3329/jsr.v5i2.13391
5. B. Ahmmad, Y. Kusumoto, M. Abdulla-Al-Mamun, A. Mihata, and H. Yang, J. Sci. Res. **2**, 1 (2010). https://doi.org/10.3329/jsr.v2i1.2660
6. F. DeSilva, Activated Carbon Filtration, Water Quality Product Magzi, Jan. 2000
7. I. Gehrke, A. Geiser, and A. Somborn-Schulz, Nanotechnol. Sci. Applicat. **8**, 1 (2015). https://doi.org/10.2147/NSA.S43773
8. The Environment Conservation Rules 1997 (Government of the People's Republic of Bangladesh Ministry of Environment and Forest, August 1997).