Soil Environ. 39(2): 165-172, 2020
DOI:10.25252/SE/2020/152168
Online ISSN: 2075-1141
Print ISSN: 2074-9546

Removal of chromium from effluent of tannery industries in Bangladesh using rice husks as natural adsorbent

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[Received:** April 4, 2020 **Accepted:** September 18, 2020 **Published Online:** October 13, 2020**]

Abstract

Nowadays heavy metals especially Cr have posed a serious threat to water bodies due to environmental pollution. The tannery industries in Bangladesh have been releasing a significant amount of Cr for years to the environment. The current research works focus on the efficient removal of Cr from tannery effluents using rice husks and coconut shell as natural adsorbents. Chromium concentration determined was 1500 mg L^{-1} which is alarmingly high in effluents just after chrome tanned discharge, and that was 1.30 mg L^{-1} Cr in effluents from dumping storage. Rice hush and coconut shell adsorbent were applied to remove Cr. Chemical modifications by treating rice husks with coconut shell increased the adsorption ability of rice husks for Cr removed. Among these adsorbents rice husks of 50 mesh size (particle size 0.297 mm) showed the maximum adsorption (98%) within 6 hours without any stirring effect. However, rice husks of 200 mesh size (particle size 0.297 mm) showed the adsorption (67%) within 6 hours with any continuous stirring effect. These results suggest that cheaply available rice husks can be considered as a good adsorbent for the removal of Cr from tannery effluents.

Keywords: Activated carbon, coconut shell, treatment, spectroscopy

Introduction

Industrial pollution is a growing environmental concern all over the world, especially in Bangladesh (Ahmed and Goni, 2010). Due to the discharge of large amount of metal-contaminated wastes from different industries, environment is being polluted by heavy metals day by day (Tchounwou *et al*., 2012). Pollution caused by heavy metals is increasing with the increased usage of chemicals in industry and agriculture (Azom *et al*., 2012). Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation in food chain as non-biodegradable pollutants (Tariq *et al*., 2005; Vellaiappan *et al*., 2002; Jenkins *et al*., 2004). Tannery converts raw hides and skins into leather for manufacturing different articles like shoes, bags, suitcases, belt, wallet, jacket and many other products. In the past, leather processing was carried out manually using certain indigenous methods. Tannery is one of the oldest and fastest growing industry in Bangladesh. There are about 214 tanneries in Bangladesh (Rahman, 2005; Tasnim *et al*., 2016; Paul *et al*., 2013). Though leather industry sector is the fourth largest foreign exchange earner of Bangladesh, it has some adverse effect on our environment. In Hazaribagh, tannery estate, about 190 tannery units have been set up in only 60 acres of land. The first thing to notice when someone walks the streets of Hazaribagh is the terrifying and seemingly all-encompassing odor of tanning chemicals. According to the Department of Environment, tanneries circulate liquid poisonous waste on Hazaribagh road as well as in running rivers, reservoirs and canals without daily treatment of 22000 cubic meters (Ahmed, 2015). Most tanneries are in Dhaka, beside the River Buriganga into which they flush their wastewater Studies have found high levels of pollution at several points in the river. Among the various organic and inorganic wastes, heavy metals are the most important factor, emitted from the tanning industries. However, due to the worrying levels of environmental pollution resulting from various tannery operations and practices, it is becoming increasingly difficult to maintain the tanneries. The main concern of tanneries effluents is increase of BOD/COD, suspended solids and heavy metal contents in the water body (Bhuiyan *et al*., 2011). Heavy metals like Cr, Hg, Pb, Cd, Cu and Ni are extremely toxic even at minute quantities (Kornhauser *et al*., 2002).

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Chromium is being released into the environment in chemically and physically apparently different forms, Cr content of wastewater generated from a variety of industries poses a serious threat to the environment. Their concentration in the environment has increased to dangerous levels due to extensive industrial activities. Industries dealing with paints, pigments, dyes, textile, leather, etc. are an important source of Cr contamination into the river. Macrophytes in the river absorb various amounts of nutrients and pollutants, but the macrophytes are then eaten by livestock or humans. Bio magnification of Cr in human body is shown in Figure 1.

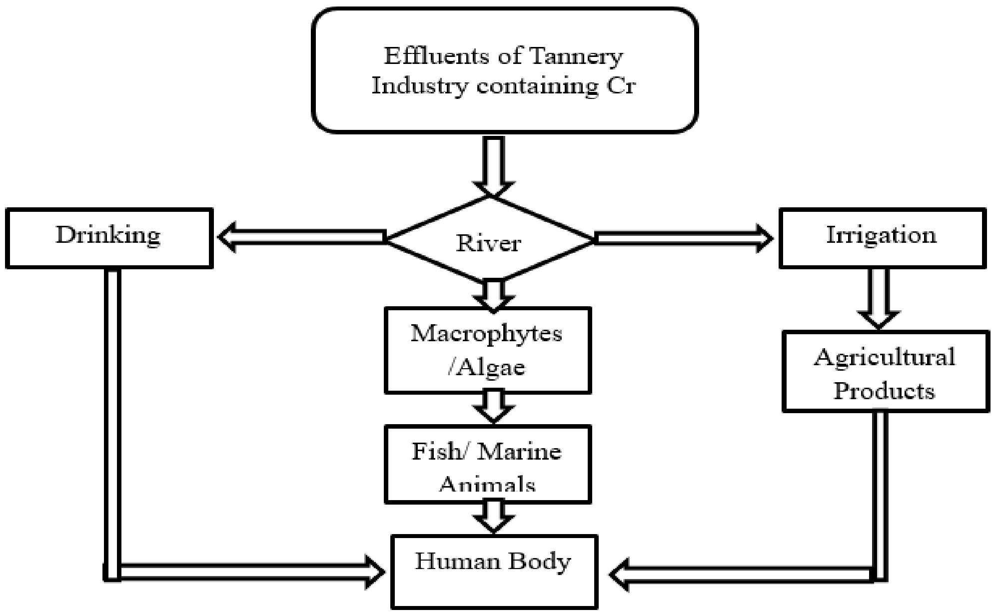

Figure 1: Heavy Metal Accumulation in Human Body

Other studies have measured heavy metal species in soil and plants in the tannery areas that have been affected by tannery waste. Cr is found in all types of the environment, including air, water, and soil, and many of its chemical forms are harmful pollutants for the environment and human health. Cr is less mobile, less toxic and is found mainly in soil and aquatic environments bound to organic matter. Despite a century of industrial use, there is still a gap in the basic knowledge of the process of activity and its effects on the major organ systems of animals and humans. The most common human side effects, other than lung cancer and death are skin rashes, stomach and ulcer worsening, respiratory problems, weakened immunity, kidney and liver damage, and changes in genetic material. Cr is recognized for enhancing the action of insulin, the decisive hormone for the metabolism and storage of carbohydrates, fats and proteins in the body. Its toxic mechanism mediates DNA strand breaks, reactive oxygen species production, and association with glutathione metabolism in living systems. Phytoremediation - the process of bioremediation that employs a variety of plants to mine, transfer, stabilize and eliminate contaminants in the soil - is important as an effective control system for crew-contaminated lands. According to WHO, more than 8,000 workers in tannery of Hazaribagh and India suffer from gastrointestinal, skin diseases and other diseases and 90% of this population dies before the age of 50. Conservative technologies for metal control are growing in interest, as they were able to remove contaminants and reuse valuable by-products as a result of waste and side flows from the manufacturing process. Removal of metals from wastewater is achieved principally by the application of several processes such as adsorption (Devi and Jayakumar, 2014;Amuda *et al*., 2007; Kumar, 2006; Marin-Allende *et al*., 2017; Sivaraman *et al*., 2009; Revathi *et al*., 2016). The search for alternative and novel treatment strategies has focused on the use of biological substances for heavy metal removal and has gained significant credibility in recent years because of the high performance and low cost of these materials (Al-Farraj, 2013; Elliss and Sekaran, 2016; Shazia *et al*., 2013; Richards *et al*., 2016). Therefore, the efforts are being directed towards the use of naturally available low-cost adsorbents for the removal of heavy metals. It is clear that this industry is one of the main sources in the country's economy, but it poses a major threat to public health and poses a serious threat to the environment. Therefore, industrial effluents that cause a wide range of environmental harm and health risks are of major concerns not only in developing countries such as Bangladesh but also in developed countries. The main objective of this study was to evaluate the presence of heavy metals in effluents of tannery industries in Bangladesh and develop a suitable method for the removal of heavy metals from tannery effluents by selecting efficient and cost effective naturally available adsorbents. The concern of this research is the heavy metals, especially chromium, present in the chemicals used during tanning and to maximize heavy metal removal efficiency and minimize pre-operational costs.

Material and Methods

The chemicals used were of analytical grade Merck, Germany and effluent sample were collected from different sample discharging zone.

Preparation of adsorbents

One gram of each collected adsorbent was burnt at 250^{0}C. Then the ash was dissolved in 50 mL distilled water and filtered. The ash was treated with concentrated nitric acid which dissolved the remaining solid particle and decolorized the solution. The NH_4OH was added in presence of NH_4Cl for ensuring whether the adsorbents contained Cr itself or not. It was found that the adsorbents were free of Cr contamination. Then the adsorbents were grinded through a grinder especially blender to fine particles. The fine adsorbents particles were screened with a 50, 100 and 200 mesh screens. The sieved adsorbents were heated at 30-32^{0}C to increase potency. Finally, they were ready for adsorption. To have a comparative study, activated carbon of 100 mesh and 200 mesh rice husks adsorbent was prepared at 450^{0}C.

Procedure

Removal of metals from effluents was carried out by adsorption process using different adsorbents (Mohan *et al*., 2005; Amuda *et al*., 2007; Sivaraman *et al*., 2009; Devi and Jayakumar, 2014; Revathi *et al*., 2016; Marin-Allende *et al*., 2017). The collected and preserved effluent samples were taken as 100 mL with 1g of different size adsorbents for same retention time (6 h) at various conditions. The whole work was done following two consecutive procedures such as:

In Procedures –I, continuous stirring was carried out through magnetic stirrer (MS7-H550-PRO) in beaker. After treating the collected sample in adsorption process by different mesh size and different sizes of activated carbon of rice husks with different temperature. After 6 h adsorption, a filtrate was obtained in each case through filtration which was taken to further analyses.

In Procedure –II, adsorbents were soaked in collected sample solution in airtight stoppered bottle. Effluent collected just after Cr tanned discharge was treated with different adsorbents of same size. After 6 h treatment, a filtrate was found in each case through filtration which was taken to further analyses.

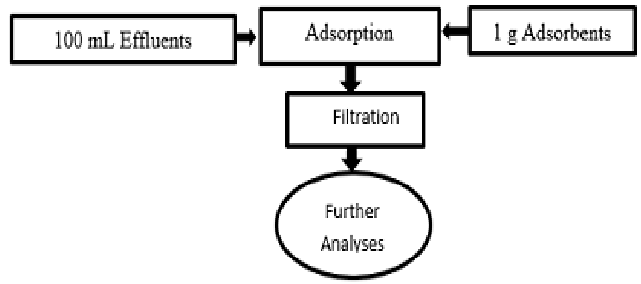

Figure 2: Working Procedure

Sampling for atomic absorption spectroscopy

The raw sample and treated samples were filtered through ash less filter paper. Then 10 mL of each sample was pipetted out to test tube.

Digestion of the samples

Each sample was treated with 1 mL concentrated HNO_3 acid for digestion of the sample. As a result, the solid particle, if any, would be dissolved, which is pre-condition for atomic absorption spectroscopy (Thermo scientific ICE 3000).

Standard sample preparation

Potassium dichromate solution of 0.5, 1, 2, 5, 7 and 10 mg L^{-1} were taken, and it was diluted to 10 mL with distilled water.

Figure 3: Standard sample preparation for AAS

Calibration for standard solution

A calibration curve of absorbance vs concentration was drawn for the standard solution absorbance; comparing with which the measuring absorbance as well as concentration of respected metal was determined.

Table 1: Chromium concentration in tannery effluent in the samples

Sample Name	Chromium Content (g L^{-1})	Removed Percentage(%)
Raw Sample	**1.30**	
After Treating with 100 Mesh Rice Husks	0.97	25.39
After Treating with 200 Mesh Rice Husks	0.80	38.47
After Treating with 200 Mesh Rice Husks at 15^0C	0.43	66.93
After Treating with 200 Mesh Rice Husks at 35^0C	0.64	50.77
After Treating with 100 Mesh Activated Carbon of Rice Husks	0.89	31.54
After Treating with 200 Mesh Activated Carbon of Rice Husks	0.88	32.31

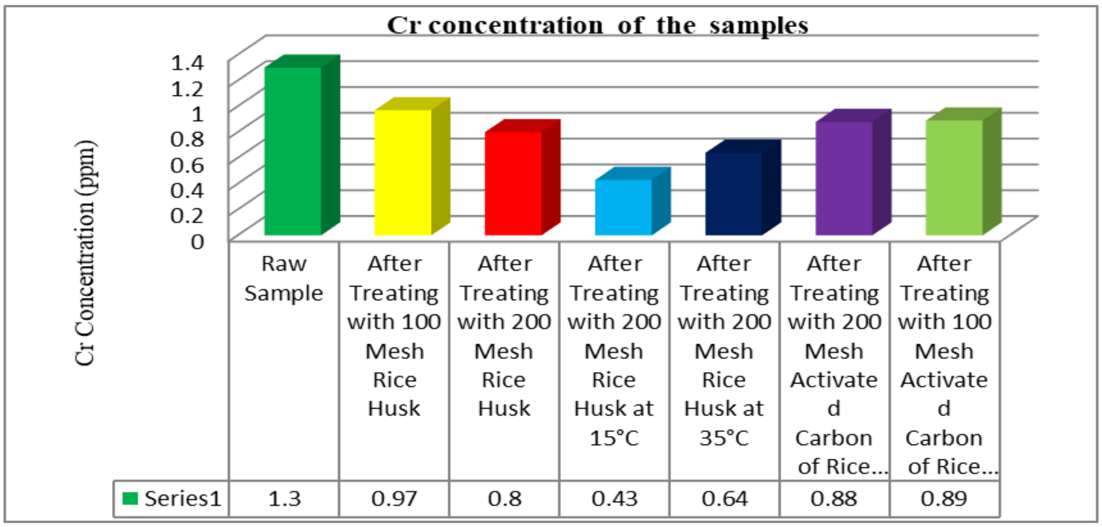

Figure 4: Chromium concentration of the tannery effluent samples

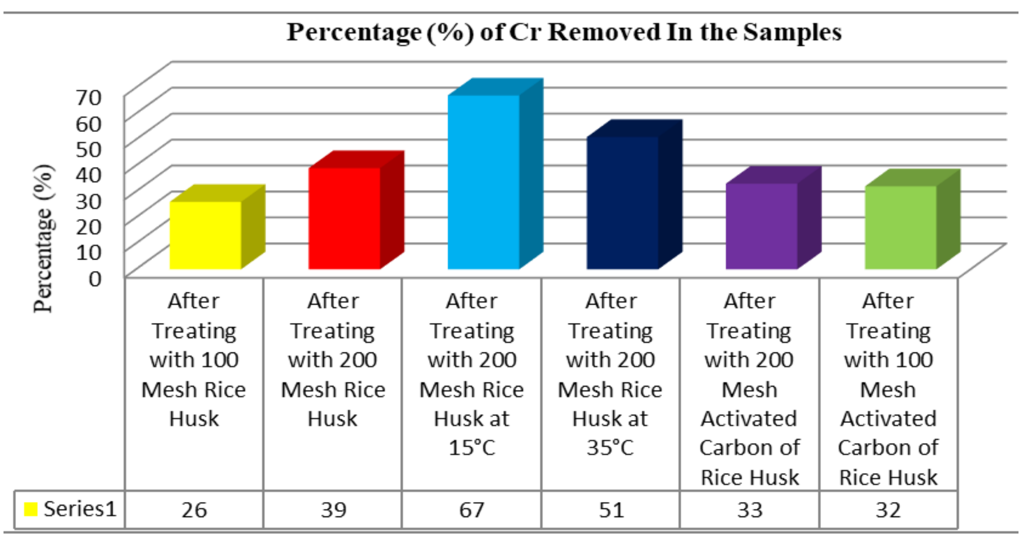

Figure 5: Effect of treatments on percentage of Cr removed in the samples

Results and Discussion

Chromium concentration in tannery effluent

Chromium is a significant contaminant of tannery effluent; it is carcinogenic and causes serious adverse effects even at minute level on marine animal as well as human being (Kornhauser *et al*., 2002; Hossain *et al*., 2007). Hence, the tannery effluents must be treated before discharge in the water bodies. Figure 4 shows the initial Cr concentration is 1.30 mg L^{-1}. To achieve a best outcome for the removal of Cr from the collected sample, it was treated under various conditions for 6 h.

In the table1**,** the data indicate the treatment of raw sample with different mesh size (100 mesh and 200 mesh) rice husks. Firstly, raw sample was treated with 100 mesh rice husks. After treatment, Cr content is 0.97 mg L^{-1} (Figure 4) which represents about 26% removal (Figure 5). Secondly, raw sample was treated with 200 mesh rice husks. After treatment, Cr content became to be 0.80 mg L^{-1} (Figure 4) and this data indicates about 39% removal (Figure 5). In this case, better adsorption was occurred through 200 mesh rice huskss. These data show that the extent of adsorption increases with the increase of surface area of the adsorbent **(**Desjonqueres and Spanjaard, 2012; Oura *et al*., 2013).

The table 1 indicates the treatment of raw sample at different temperatures (15^0C and 35^0C) with 200 mesh rice husks. Initially, the raw sample was treated with 200 mesh rice husks at 15^0C. After treatment, the Cr content was 0.43 mg L^{-1} (Figure 4) which represents about 67% removal (Figure 5). Then the raw sample was treated with 200 mesh rice husks at 35^0C. The Cr content becomes 0.64 mg L^{-1} (Figure 4) and this data shows about 51% removal (Figure 5). In this case, more acceptable adsorption was found by 200 mesh rice husks at 15^0C. These data indicate physical adsorption occurs more readily at lower temperature and decreases with increase in temperature (Desjonqueres and Spanjaard, 2012; Oura *et al*., 2013).

The data regarding the adsorption of raw sample with different sizes of activated carbon of rice husks is shown in table 1. At first, the raw sample was treated with 200 mesh activated carbon of rice husks. After adsorption, the Cr content is 0.88 mg L^{-1} (Figure 4) and this data indicates 33% removal (Figure 5). Secondly, raw sample was treated with 100 mesh activated carbon of rice husks. After treatment, the Cr content becomes 0.89 mg L^{-1} (Figure 4) and this data represents about 32% removal (Figure 5). In this case, slightly better adsorption was observed by 200 mesh activated carbon of rice husks. Though a sharp difference is found between 100 mesh and 200 mesh activated carbon. This data is promising and indicating the extent of adsorption slightly increases with the increase of surface area of the activated carbon **(**Akter and Tunali, 2005; Amuda *et al*., 2007).

Heavy metal (chromium) content in the samples

The Cr concentration in effluent collected just after chrome tanned discharge is 1500 mg L^{-1} (Table 2). This data represents highly adverse pollution of the effluent, whereas Cr presence at minute level can cause serious health effect (Kornhauser *et al*., 2002; Hossain *et al*., 2007). Hence, the raw sample was treated with different adsorbents of same size for 6 h. Firstly, the raw sample was treated with 50 mesh rice huskss. After treatment, Cr content is 20.5 mg L^{-1} (Figure 6) which represents about 98% removal (Figure 7). Secondly, raw sample was adsorbed in 50 mesh rice huskss. After treatment, Cr concentration became 424.25 mg L^{-1} (Figure 7) and this data indicates about 71% removal (Figure 7). In this case, better adsorption occurred through 50 mesh rice huskss. This data indicates better adsorption capacity of same size rice husks than coconut shell. If it could be possible to know the porosity or active sites of rice husks and coconut shell, the reason behind better adsorption capacity of rice husks than coconut shell could have been understood (Sivaraman *et al*., 2009). It was observed that more acceptable results were obtained in adsorption without stirring than adsorption with continuous stirring**.** Though more increased surface area of adsorbent was applied in adsorption with continuous stirring, expected results might be hampered due to some reasons such as –The Heavy Metal's (Cr) particles exist in the sample solution as micro level; the continuous stirring could interrupt proper contact between solid phase (adsorbents molecules) and liquid phase (existing ions).The beaker used for adsorbing solution was not so air tight which might affect the expectation as pressure played a vital role in adsorption process (Desjonqueres and Spanjaard, 2012; Oura *et al*., 2013).

On the contrary to adsorption without stirring, airtight stoppered bottle was used as closed media of adsorption**,** which retain exerted pressure from the process and adsorption facilitated in this condition (Desjonqueres and Spanjaard, 2012; Oura *et al*., 2013). Absence of stirring could allow the adsorbing substituents to have better contact facility and get adsorbed. These could be the reasons behind the more acceptable results in adsorption without stirring than adsorption with continuous stirring. From the above comparative discussion, it can be noticed that this work is more cost effective as well as promising to remove Cr from tannery effluents using rice husks as an adsorbent.

Table 2: Heavy metal (chromium) content in the samples after treating with different adsorbents of same size

Sample Name	Chromium Content (mg L^{-1})	Removal Percentage (%)
Raw Sample	1500	
After Treating with 50 Mesh Rice Husks	20.5	98
After Treating with 50 Mesh Coconut Shell	424.25	71

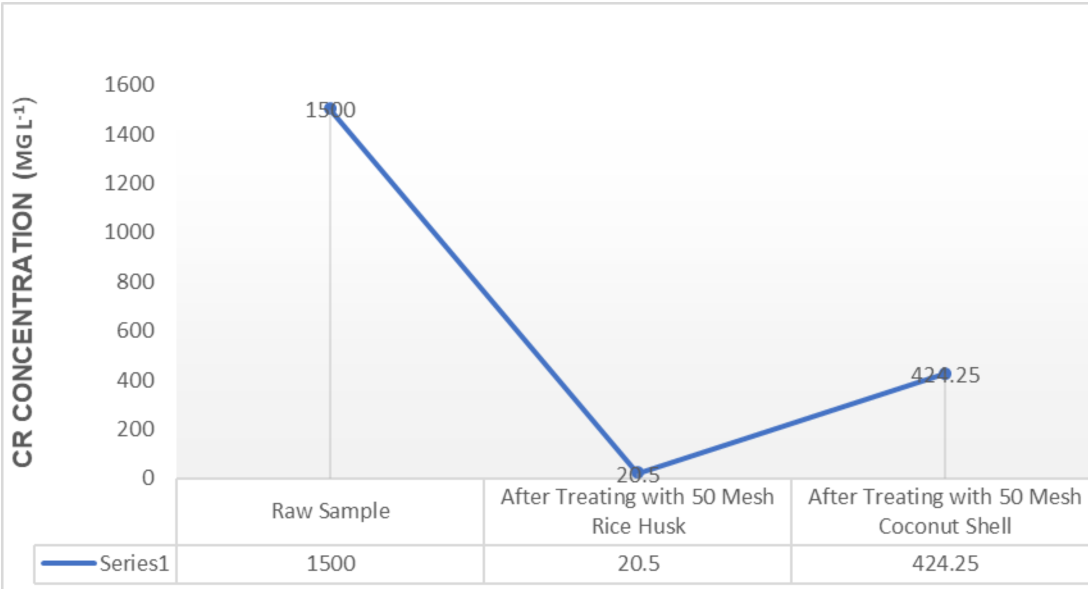

Figure 6: Effect of adsorbents of Cr content in the sample

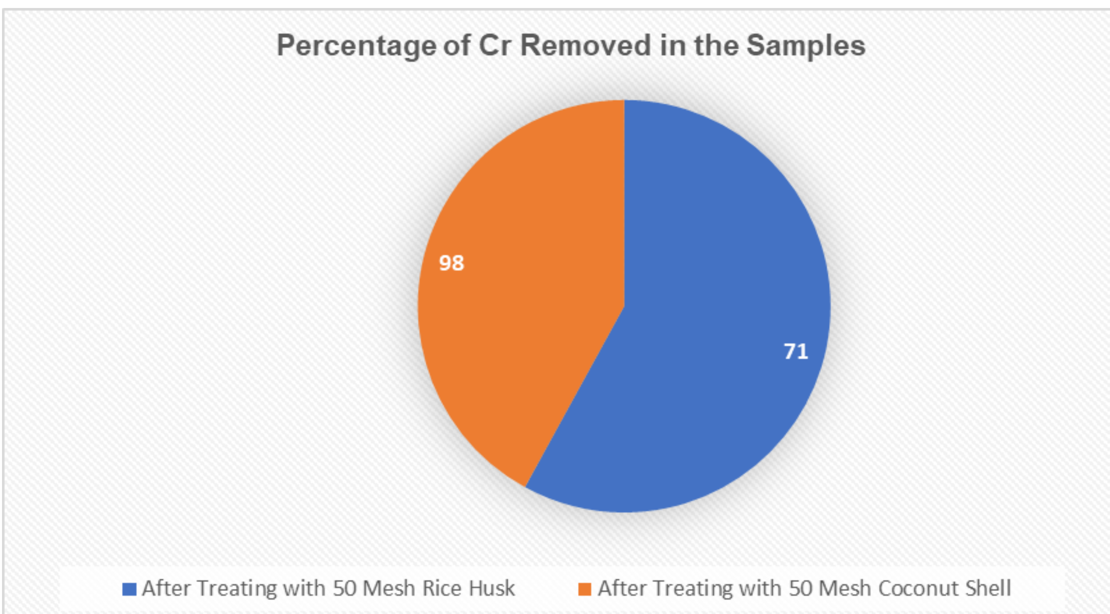

Figure 7: Percentage of Cr removed in the samples

Conclusions

A suitable method has been developed for the estimation and removal of Cr concentration from tannery effluents collected from Savar New Tannery Estate and its surrounding areas. It was found that natural adsorbents (rice husks, coconut shell) remained very effective to remove Cr from tannery effluents by physical adsorption, Maximum adsorption of 98% was achieved by using 1 g of 50 mesh (particle size 0.297 mm) rice hush as adsorbent without stirring within 6 h. Physical characteristic were found well below the prescribed permissible limits for effluent discharge. Whenever the effluent is treated at lower temperature (15^0C) in adsorption with continuous stirring for 6 h using 1g of 200 mesh (particle size 0.074 mm) rice husks, about 67% Cr concentration is removed. After treatment, corresponding physical parameters were found very close to acceptable limit. Though these data indicate promising results, further efforts are still required in order to maximize Cr removal efficiency and minimize preoperational costs.

Acknowledgments

Special thanks to managers of the different tannery industries in Savar New Tannery Estate for providing the tannery effluents.

References

Ahmad, J.U. and M.A. Goni. 2010. Heavy metal contamination in water, soil, and vegetables of the industrial areas in Dhaka, Bangladesh. *Environmental Monitoring and Assessment* 166(1-4): 347-357.

Ahmed, P. 2015. Reinforcing recruitment and selection in public sector manufacturing corporations of Bangladesh: A case study on Bangladesh chemical industries corporation (BCIC). *Management* 29(3-4).

Al-Farraj, A.S. 2013. Assessment and heavy metal behaviors of industrial wastewater: A case study of Riyadh city, Saudi Arabia. *Proceedings of the International Academy of Ecology and Environmental Sciences* 3(3): 266.

Amuda, O.S., A. Giwa and I.A. Bello. 2007. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal* 36(2): 174-181.

Azom, M.R., K. Mahmud. S.M. Yahya, A. Sontu and S.B. Himon. 2012. Environmental impact assessment of tanneries: A case study of Hazaribag in Bangladesh. *International Journal of Environmental Science and Development* 3(2): 152.

Bhuiyan, M.A.H., N.L Suruvi, S.B. Dampare, M.A. Islam, S. Ganyaglo and S. Suzuki. 2011. Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh. *Environmental Monitoring and Assessment* 175(1-4): 633-649.

Desjonqueres, M.C. and D. Spanjaard. 2012. Concepts in surface physics. Springer Science & Business Media. Berlin, Germany.

Devi, B.M. and K. Jayakumar. 2014. Phytoremediation studies on tannery effluent using pilot scale constructed wetlands. *Hydrology and Watershed Management: Ecosystem Resilience-Rural and Urban Water Requirements* 1: 365.

Elliss, R. and V. Sekaran. 2016. COD removal efficiency of activated carbon adsorbent for tannery wastewater treatment. *International Journal for Innovative Research in Science & Technology* 5 (5): 18213-18215.

Hossain, A.M., T. Monir. A.R. Ul-Haque, M.A.I. Kazi, M.S. Islam and S.F. Elahi. 2007. Heavy metal concentration in tannery solid wastes used as poultry feed and the ecotoxicological consequences. *Bangladesh Journal of Scientific and Industrial Research* 42(4): 397-416.

Jenkins, R., J. Barton and J. Hesselberg. 2004. The global tanning industry: a commodity chain approach. Environmental Regulation in the New Global Economy: the impact on industry and competitiveness. *Asia Pacific Journal of Environmental Law* 157-172

Kornhauser, C., K. Wrobel, J.M. Malacara, L.E. Nava, L. Gomez and R.Gonzalez. 2002. Possible adverse effect of chromium in occupational exposure of tannery workers. *Industrial Health* 40(2): 207-213

Kumar, U. 2006. Agricultural products and by-products as a low-cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essays* 1(2): 33-37.

Marín-Allende, M.J., E.T. Romero-Guzmán, J.J. Ramírez-García and L.R. Reyes-Gutiérrez. 2017. Chromium (VI) removal from aqueous medium by maize cane and agave bagasse biomasses. *Particulate Science and Technology* 35(6): 704-711.

Oura, K., V.G. Lifshits, A.A. Saranin, A.V. Zotov and M. Katayama. 2013. Surface Science: An Introduction. Springer Science & Business Media. Berlin, Germany.

Paul, H. L., A.P.M. Antunes, A.D. Covington, P. Evans and P.S. Phillips. 2013. Bangladeshi leather industry: An overview of recent sustainable developments. *Journal of the Society of Leather Technologists and Chemists* 97(1): 25-32.

Rahman, M.A. 2005. Sub-contracting Programme of Bangladesh Small and Cottage Industries Corporation (BSCIC)-An Overview. *Pakistan Journal of Social Sciences* 3(6): 892-897

Revathi, A., A. Thaminum, S. Ulaganathan and C. Ravichandran. 2016. Adsorption and discoloration on tannery effluents using various metal chloride samples collected near tannery industry. *International Journal of Applied and Advanced Science Research* 1(2): 2456-3080.

Richards, A., V. Chandrakumar and G. Prabhakaran. 2016. Renowned treatment methods and identification of tannery waste with engineering safety and regulatory laws. *Journal of Chemical and Pharmaceutical Sciences* 442-446

Shazia, I., S. Uzma and A. Talat. 2013. Bioremediation of heavy metals using isolates of filamentous fungus Aspergillus fumigatus collected from polluted soil of Kasur, Pakistan. *International Research Journal of Biological Sciences* 12 (2): 66-73.

Sivaraman, B., K.P. Fears and R.A. Latour. 2009. Investigation of the effects of surface chemistry and solution concentration on the conformation of adsorbed proteins using an improved circular dichroism method. *Langmuir* 25(5): 3050-3056.

Tariq, S.R., M.H. Shah, N. Shaheen, A. Khalique, S. Manzoor and M. Jaffar. 2005. Multivariate analysis of selected metals in tannery effluents and related soil. *Journal of Hazardous Materials* 122(1-2): 17-22.

Tasnim, F., I. Rahman, M. Rahman and R. Islam. 2016. A review on occupational health safety in Bangladesh with respect to Asian Continent. *International Journal of Public Health and Safety* 1: 102.

Tchounwou, P. B., C.G. Yedjou, A.K. Patlolla and D.J. Sutton. 2012. Heavy metal toxicity and the environment. P.133-164. In: Molecular, Clinical and Environmental Toxicology. A. Luch, (ed.). Springer, Basel.

Vellaiappan, A., G. Melchias and P. Kasinathan. 2002. Effect of heavy metal toxicity on the nodulation pattern of legume cultivars. *Ecotoxicology and Environmental Safety*- Journal 12(1): 17-20.