Advance Research in Textile Engineering

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Research Article

Feasibility Study on the Reduction of Phenol and Chlorophenol Concentration from the Contaminated Textiles Using Suitable Detergent and Dispersing Agent

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Received: May 04, 2020; **Accepted:** May 27, 2020; **Published:** June 03, 2020

Abstract

Compliance is a buzz word now-a-day every industry is very much concerned about sustainable development. An investigation has been carried out with the aim of reducing the concentration of phenol & chlorophenols from the contaminated textiles (polyester & polyamide) within the acceptable limit according to the standard 100 by Oeko-Tex using suitable detergent and dispersing agent. The results were studied in comparison with the contaminated textiles and chemical treated one using 5g/l and 10g/l dosing of nonionic detergent and dispersing agent together with the help of GC-MS & GC-ECD (Gas chromatography-Electron capture detector) and HPLC (High Performance Liquid Chromatography) for chlorophenols and phenol respectively. Color fastness to wash and rubbing properties were also compared between untreated and after treated goods. Color fastness to wash & rubbing found slightly better than the contaminated one. The concentration (mg/kg) of phenol & chlorophenols successfully drop down from the limit exceeding point to the permissible limit given by the standard 100 by Oeko-Tex.Moreover, the used chemicals found free of toxic APEOS. Finally, this process found as an easier solution while facing such kind of phenol and chlorophenols contamination problem to comply with different international compliance legislations.

Keywords: Detergent; Dispersing agent; Phenol; Chlorophenol; mg/kg

Introduction

Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. Generally, five types of chlorophenols are found, such as Monochlorophenol (MCP), Dichlorophenol (DCP), Trichlorophenol (TCP), Tetrachlorophenol (TeCP) & Pentachlorophenol (PCP) with their isomers [1]. Among all of the chlorophenols, only the dichlorophenol (2-chlorophenol) is available in the liquid form at room temperature while all the other chlorophenols are available in the solid state [1-3]. Chlorophenols are commonly used as preservatives for the production of textile auxiliaries. Very often these can also be used as raw materials to produce synthetic dyes [3]. Later, when these auxiliaries and dyes are used at different stages of the textile wet-processing, the textiles are contaminated along with the produced wastewater [1]. Print paste is also a source of chlorophenols that can cause contamination to the textiles also [4]. Dispersing agent used for the dyeing of polyester as a carrier for the dyes to the fiber is also a source for chlorophenols [5]. Phenol comes from fixing agent, used to treat polyamide fiber after dyeing in order to increase the colour fastness to wash. During synthetic fibers like- polyamide, polyester processing sometimes- such problem also creates difficulties to the dyers to be compliant with the Restricted Substance List (RSL) guidelines provided by the retailers [6]. Since these organic compounds are carcinogenic, hence, possessing several adverse health effects and are strictly restricted to use up to a permissible limit for textiles [7, 8]. Some chlorophenols can be very toxic to aquatic organisms and above certain exposure, may cause long-term adverse effects in the aquatic environment [6,9]. Besides, while using above the prescribed levels and due to the long-term exposure, some chlorophenols may result in the development of particular cancers, inhalation issues and dermatological problems [8,10-12]. Each of these isomers has different permissible exposure levels. Some chlorophenols are toxic to the aquatic environment while others are carcinogenic & can cause systemic organ toxicity [8,10]. According to Oeko-Tex guideline, textile and leather materials should contain <0.05mg/kg of each TeCP & PCP and <0.5mg/kg of each TCP [8,13]. Similarly, standard 100 by Oeko-Tex has also norms for the permissible exposure limits of chlophenols & phenol. For phenol, maximum permissible limit is <20mg/kg [8,13]. However, according to standard 100 by Oeko-Tex the maximum exposure limit has different acceptable ranges for four different product classes of i-iv [9]. Since Oeko-Tex is applied for finished product so once any contamination happens it does need to test from the fiber processing to the finished article [6,9]. Other than these different retailers have different permissible exposure limit mentioned their RSL (Restricted Substances List) guideline. Researchers already did few investigations to remove these toxic substances, which are responsible for endocrine disruption and many other adverse health effects for human being as well as aquatic life due to their persistence capability. For example. Soybean peroxidase and excilamp have the potential to reduce 4-chlorophenol successfully [14]. Another study demonstrated that the use of soybean hulls and hydrogen peroxide can produce certain enzyme that can reduce both phenol (96%) and 2-chlorophenol (98.5%) from the wastewater in the presence of

Citation: Md Salauddin SK and Md Faruque AAl. Feasibility Study on the Reduction of Phenol and Chlorophenol Concentration from the Contaminated Textiles Using Suitable Detergent and Dispersing Agent. Adv Res Text Eng. 2020; 5(1): 1046.

detergent [15]. Besides, advanced oxidation process is also reported to reduce the chlorophenols and alkylphenol ethoxylates [16]. While inexpensive adsorbents produced from industrial wastes have the potential to reduce phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol [7]. Membrane technology found as the best option other than the adsorption, oxidation & biological methods to reduce phenolic compounds [17]. Flocculation and coagulation method are another physico-chemical process that can remove phenolic compounds using suitable chemicals [18]. Ozonation process can also remove phenol from polluted water [4]. Another study revealed that ozonation can reduce 2,4 dichlorophenol concentration while increase chloride [19]. Lin et al., reported that 2-chlorophenols can be degraded by the copper doped titanium dioxide with the help of visible light through photocatalytic action [20]. Fluidized bed reactor using activated carbon collected from coconut shell can successfully reduce phenol concentration up to 96% [21].The presence of external chloride can lead to a 47-fold increment in degradation rates of 4-chlorophenol than those in the absence of chloride in UV/peroxymonosulfate process [22].

Although there are distinct constitutions for both the finished goods and wastewater, researchers are using different techniques or tools to reduce or degrade these toxic substances concentration. Globally, chemical industries are utilizing 4 million types of chemical substances in their processing routes, while textile industries are familiar with 600 toxic substances [23]. Textile industries are using significant amounts of phenolic compounds throughout different processing cycle depending on the finished product. The use of these harmful substances over permissible limit banned by different international legislations. For textile industry, retailers as well as different international certification bodies have their own manufacturing Restricted Substance Lists (RSL) with acceptable exposure limit. For the finished textiles, the phenol and chlorophenols concentration tested to confirm cumulative exposure concentration of total used chemicals during the full processing cycle. Since this branch of research over looked by the scientists considering this an attempt has been carried out to investigate how to reduce the phenolic compound from contaminated textiles. Careful selection of suitable dispersing agent and detergent was crucial that have the potential to do the job without impairing the goods quality.

Until now, most of the research mainly based on removal of the phenolic issues from the industrial wastewater, overlooking the presence of this in the finished textiles. Therefore, in this current study, we arefocusing on the removal of these phenolic issues from the contaminated textiles instead of the wastewater.

Materials and Methods

Materials

The disperse dyed single-jersey plain knitted fabric having composition of 80% polyester and 20% spandex with areal density of 220g/m^2 was supplied by a textile industry “Network clothing, Bangladesh”. 100% nylon 6 tape (0.5 cm) dyed by acid dyes was provided by Naturub associates, Bangladesh. The digital image of all the samples used in this study has been shown in Figure 1. Since all the samples were in finished state, these were directly used for the chemical treatment to reduce the chlorophenol and phenol concentration respectively without any further treatment. Commercially available detergent and dispersing agent were collected from Euro Dye Ctc and Zschimmer & Schwarz Gmbh, respectively. The multi-fiber adjacent fabric of DW type (SDC, UK) and crocking cloth (James heal, UK) were used for the testing of color fastness to washing and color fastness to rubbing. The grey scale (James heal, UK) was used for the assessing of the color fastness to wash and color fastness to rubbing test results. The OBA free non-phosphate detergent (SDC, UK) & sodium carbonate (Merck) used for assessing wash fastness.

Experimental

Chemical processing is carried out in exhaust method using laboratory-dyeing machine named AHIBA IR (DATACOLOR, USA). The machine has a capacity of 19 pots of each 300ml volume heated by infrared mechanism with the help of three fixed lamps. The pots were prepared in a liquor ratio of 1:10 with a chemical dosing of 5g/l & 10g/l described in Table 1. For both of detergent and dispersing agent in each case. The machine started running at rpm of 35 to raise temperature 60°C with a gradient of 5°C/min and continued running for 20 minutes. After that, the samples rinsed with cold water thoroughly. Finally, dried with an oven (James heal, UK) at a temperature of 80°C for 10 minutes.

Analytical study

For chlorophenol concentration test, the samples were analyzed by GC-MS & GC-ECD (Bruker Avance, USA) technique through the extraction with KOH following DIN EN ISO 17070:2007 principle. Moreover, for phenol concentration determination by HPLC (PerkinElmer, USA) following EN ISO 13365 principle. FT-IR (Perkin Elmer, USA) used to determine the functional group present in the detergent and dispersing agent. Further the toxic APEOS concentration of the detergent and dispersing agent analyzed with the LC-MS (Bruker Avance, USA).

Fastness analysis

Color fastness to wash and rubbing were evaluated according to ISO 105- C03 & ISO 105- X12 respectively. For color fastness to wash test use GYRO WASH[2] (James heal, UK) and for color fastness to rubbing CROCK MASTER (James heal, UK) respectively.

Results and Discussion

Chemical treatment analysis

As already discussed, that the PCPs are widely used as preservative for the formulation of textile chemicals to protect them from fungal growth and bacterial attack. The GC-MS analysis demonstrated the concentration of PCP in the contaminated tape as well as in the after treated one. The result clearly represents that the concentration of PCP in the contaminated nylon tape was higher than the chemicals treated tape. With the increase of chemical dosing (detergent& dispersing agent), the concentration drops down gradually. The data shows that the concentration of PCP in the contaminated tape was 0.31mg/kg which is within the acceptable limit for product class II (Skin contact items) but exceeds the limit for product class I (Baby wear) of 0.05mg/kg set by the standard 100 by Oeko-Tex [9]. The concentration comes down to 0.24mg/kg and 0.1mg/kg respectively with the treatment of 5g/l and 10g/l chemical dosing (Figure 2).

Like the PCPs, the TeCP was also used as preservative in

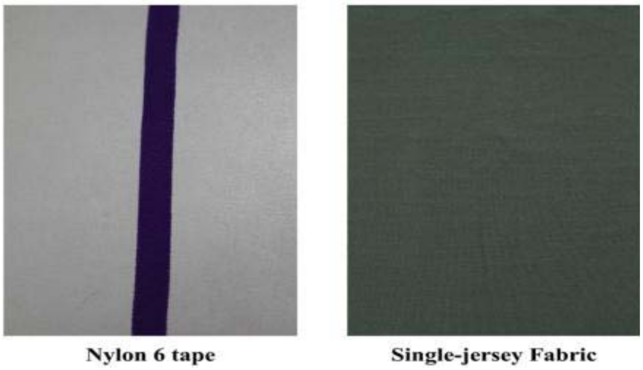

Figure 1: The digital image of the samples used in this study.

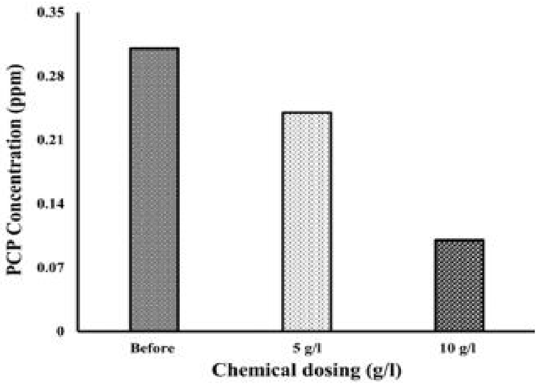

Figure 2: PCP concentration with different chemical dosing.

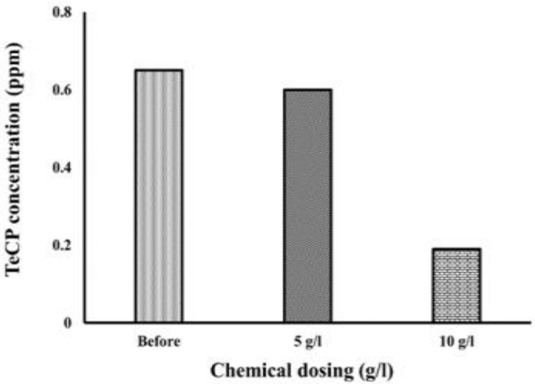

Figure 3: TeCP concentration with different chemical dosing.

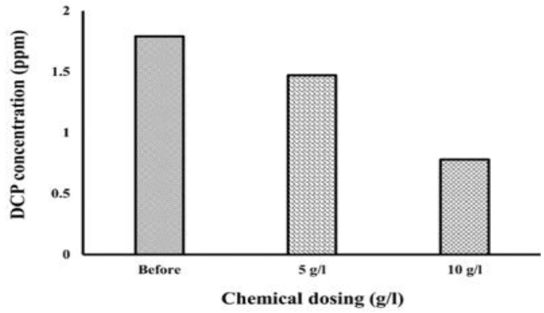

Figure 4: DCP concentration with different chemical dosing.

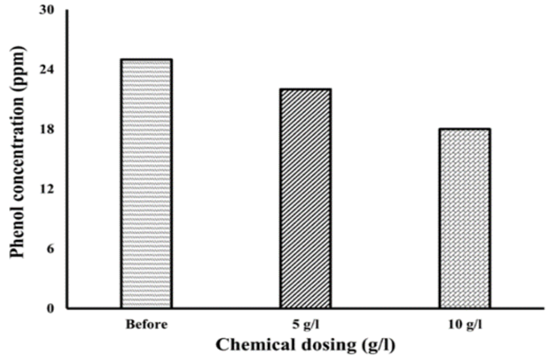

Figure 5: Phenol concentration with different chemical dosing.

the chemical formulations. The GC-MS data demonstrates the concentration of TeCP in the tape before and after of the chemical treatment. The result visualizes that the concentration of TeCP in the contaminated nylon tape was greater than the chemical treated one. As the chemical dosing (detergent & dispersing agent) increases, the concentration of TeCP goes down consistently. The result shows that the concentration of TeCP in the contaminated tape was 0.65mg/kg, which is beyond the acceptable limit set by the Oeko-Tex [9]. After the chemical treatment with the dosing of 5g/l, the concentration fall down to 0.6mg/kg which still exceeds the limit value of 0.5mg/kg recommended for product class II (Skin contact items) and 0.05mg/kg for product class I (Baby wear). Thereafter, further increasing chemical dosing to 10g/l gives better result of 0.19mg/kg which lies within the acceptable limit for product class II (Figure 3) [9].

The acceptable limit value of DCP for the product class I is 0.5mg/kg whereas for product class II it is 3.0mg/kg. From the analyzed data of GC-MS represents that the DCP concentration in the contaminated tape was 1.79mg/kg, which declined gradually to 1.47mg/kg with the treatment of 5g/l chemical dosing however further increased dosing of 10 g/l the concentration drops down to 0.78mg/kg (Figure 4).

The phenol is supposed to be carcinogenic. Like the chlorophenols, phenol is also restricted to be used beyond the permissible limit for textile processing. The acceptable limit value of phenol for the product class I is 20mg/kg though it should be below 50.0 mg/kg for product class II. HPLC analysis results shows that the phenol concentration in the contaminated polyester fabric was 25mg/kg which drop down gradually to 22mg/kg with the treatment of 5g/l chemical dosing however further increased dosing of 10 g/l the concentration drops down to 20mg/kg (Figure 5).

From the analysis of overall data, it is clearly noticed that the concentration of phenol and chlorophenols decreased for all cases, what happened for the inherent property of dispersing agent to disperse and detergent that removes the dispersion from the bath, ultimately makes it happen to lower the contamination from the contaminated textiles.

Performance analysis of detergent

Detergents are generally blend of different surfactants formulated such a way having superior cleansing property and water solubility.

Table 1: Chemical processing recipe.

Substrate	Recipe 1	Recipe 2	Recipe 3	Recipe 4
Polyester blend fabric	Detergent-5g/l Dispersing agent-5g/l	Detergent-10g/l Dispersing agent-10g/l	-	-
Nylon 6 tape	-	-	Detergent-5g/l Dispersing agent-5g/l	Detergent-10g/l Dispersing agent-10g/l

Table 2: Color fastness to wash.

Color fastness to wash								
Substrate	Samples	Color change	Color staining					
			Di-acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Polyester	Before	4	4	4-5	4	4	4-5	4-5
	Treated with recipe 1	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Treated with recipe 2	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Polyamide	Before	4	4-5	4-5	4-5	4-5	4-5	4-5
	Treated with recipe 3	4	4-5	4-5	4-5	4-5	4-5	4-5
	Treated with recipe 4	4	4-5	4-5	4-5	4-5	4-5	4-5

Inherently these chemicals have hydrophilic and hydrophobic part in their structure for effective outcome. Chemically detergents are usually alkylbenzene sulfonates and few more derivatives. The detergent used in this study composed of the careful selection of readily biodegradable nonionic and anionic surfactants that confirms better rewetting and contributes to excellent soil dispersing characteristics thus preventing redeposition of particulate matter onto the fiber as well as machine surface, once they have been pulled out. The surfactants blend successfully reduced the phenol and chlorophenol concentration (Figure 2-5) by emulsification and disassociation from contaminated textiles. Oligomers creates lots of processing difficulties while processing polyester goods. The benefits associated with the detergent confirms better fastness properties (Table 2&3) as well as the reduction of phenolic component from the treated goods.

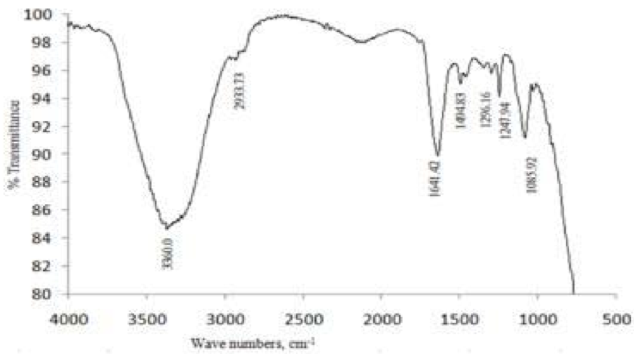

Figure 6: FT-IR spectrum of the detergent.

APEO Concentration Test: Moreover, toxicological profile of the used detergent is also important because there is always chance of the presence of APEOS in the formulation if not engineered carefully thus tested to determine the process sustainability. The AP (Alkyl Phenol) and APEOS (Alkyl Phenol Ethoxylates) responsible for endocrine disruption and restricted to add in the chemical formulation over acceptable limit. Therefore, tested according to the standard ISO 18254:2016 method with the help of LC-MS considering detection limit of 3mg/kg and found free of these toxic substance contaminations.

FT-IR Spectroscopy: FT-IR spectroscopy is widely used to determine the specific functional group present in a chemical formulation. The samples tested in ATR mode with instrument set up of 50 times scanning and resolution frequency interval of 4cm^{-1}.The FTIR spectrum of the detergent reveals the presence of -OH stretching of alcohols and phenols, C-H and -C=C-stretching of alkanes, C=O stretching vibration, aldehyde and ketones bending of C-C-C- (Figure 6).

Performance analysis of dispersing agent

It is quite easy to predict that dispersing agent is responsible for better bath dispersion. There are varieties types of commercial dispersing agent available like - polyacrylate, sodium salt of naphthalene sulphonic acid, combination of nitrogen derivative with carboxylic acid and phosphonates etc. These products have positive influence on bicarbonate problem that creates spot on the goods during processing. Solubility and agglomeration are opposite of each other as the dispersing agents prevents agglomeration thus improves solubility of the dispersed particles present in the bath. These properties of the product ultimately helped to decrease the phenolic component concentration (Figure 2-5) comes from contaminated textiles. Once the toxic components dispersed by the dispersing agents further cleaning action of detergent improves fastness property (Table 2&3) also.

For the dispersing property test 1g/l of C.I. reactive blue 21 dye stuff taken in a beaker then add 1g/l dispersing agent and heat for 20 minutes at 80°C. Once the heating completed, the dye solution filtered with Whatman filter paper. Finally, the paper assessed under microscope and found superior dispersion of dyestuff having dispersing agent in the bath than the bath contained no dispersing agent (Figure 7).

APEO Concentration Test: Likely to the detergent there is always chance of the presence of APEOS in the formulation of dispersing agent hence tested to meet the chemical compliance. Testing done according to the standard ISO 18254:2016 method considering the detection limit of 3mg/kg and confirmed free of these harmful substances.

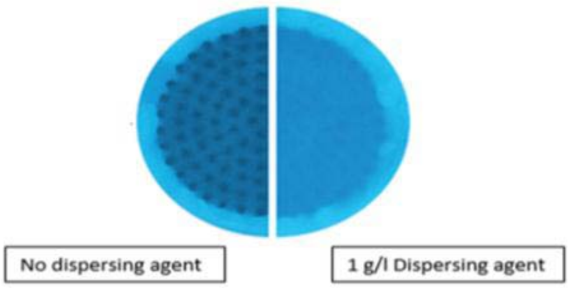

Figure 7: Dispersing property test of dispersing agent.

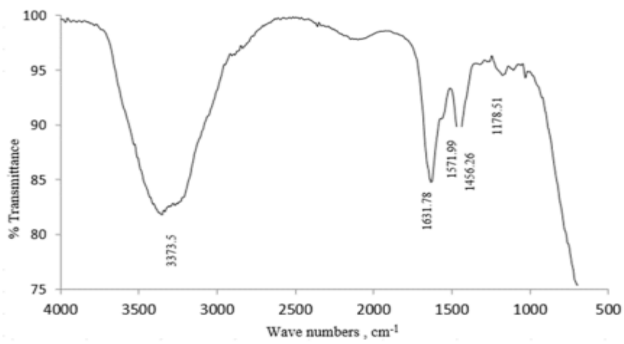

Figure 8: FT-IR spectrum of the dispersing agent.

Table 3: Color fastness to rubbing.

Substrate	Samples	Wet	Dry
Polyester	Before	3-4	4-5
	Treated with recipe 1	4	4-5
	Treated with recipe 2	4	5
Polyamide	Before	3	4-5
	Treated with recipe 3	3-4	4-5
	Treated with recipe 4	3-4	4-5

FT-IR Spectroscopy: The FTIR spectrum of the dispersing agent unveils the existence of -OH stretching of alcohols and phenols, -C=C- stretching of alkenes, primary amines (-NH_2) bending, -C-N stretching vibration, C-O stretching vibration of alcohols (Figure 8).

Color fastness analysis

The color fastness to washing (Table 2) was assessed with the help of grey scale. The fastness property of polyamide tape not affected after chemical treatment means no improvement nor degradation. The staining rating of untreated polyester fabric found 4 in the di-acetate, nylon, polyester portion of multi-fiber whereas in the cotton, acrylic, wool found 4-5. After the treatment of 5g/l chemical dosing the staining rating found 4-5 in the di-acetate, nylon, polyester portion of multi-fiber and in the cotton, acrylic, wool found 4-5. Which means half grade improvement for di-acetate, nylon & polyester portion and the cotton, acrylic & wool remains the same 4-5. While further increase of chemical dosing does not affect staining behavior. On the other hand, color change found 4 & 4-5 before and after treatment.

Like the color fastness to wash, color fastness to rubbing (Table 3) also improves by half grade. Before treatment, the dry rubbing grade was 4-5 but after treated with 10g/l it improved to grade 5. Similarly, the wet rubbing found 3, which becomes 3-4 after the treatment. This was happened due to wash out of unfix dyes by the dispersing agent & detergent from the fabric surface. As dispersing agent works behind the dispersion of dye and detergent act as a cleaning booster to remove the unfixed dyes, led to the improve of the overall fastness.

Conclusion

The experimental result reflects the extraordinary reduction of phenol and chlorophenols concentration from contaminated textiles made of polyester blend and nylon 6. This process successfully decreased the phenol and chlorophenol concentration within the acceptable exposure limit set by Oeko-Tex standard. Moreover, the process also has positive effect on color fastness to wash and rubbing. Furthermore, the used chemicals are free from toxic APEOS, which are also prohibited that confirms overall process sustainability. The nonionic detergent and anionic dispersing agent have the ability to work against such type of contamination reduction. Finally, this process can act as an aid for the industry while facing such type of problems.

Funding

This is a self-funded research work. The authors did not receive any financial assistance and support from any type of organizations.

Acknowledgement

I would like to thank Harris and Menuk (BD) limited for allowing me to utilize the laboratory facilities for this research work.

References

1. Musteret CP, Cailean D, Barjoveanu G, Teodosiu C. “An assessment of operational parameters for the removal of chlorophenols from wastewater,” Environmental Engineering & Management Journal (EEMJ). 2010; 9: 1451-1457.
2. I Sciences International and RT Institute. Toxicological Profile for Chlorophenols. US Department of Health and Human Services, Public Health Service, Agency. 1999.
3. Stouten H, Bessems JG. “Toxicological profile for obenzylpchlorophenol,” in Journal of Applied Toxicology: An International Forum Devoted to Research and Methods Emphasizing Direct Clinical, Industrial and Environmental Applications. 1998; 18: 271-279.
4. Turhan K, Uzman S. “Removal of phenol from water using ozone,” Desalination. 2008; 229: 1-3.
5. Ghaly A, Ananthashankar R, Alhattab M, Ramakrishnan V. “Production, characterization and treatment of textile effluents: a critical review,” J Chem Eng Process Technol. 2014; 5: 1000182.
6. Salerno-Kochan R, Kowalski M. “Safety Management of Textile Products in the European Union and Estimation of its Efficiency. Part 2”. FIBRES & TEXTILES in Eastern Europe. 2020; 28: 141.
7. Jain AK, Gupta VK, Jain S, Suhas. “Removal of chlorophenols using industrial wastes”. Environmental science & technology. 2004; 38: 1195-1200.
8. Foundation Z. ZDHC MRSL V2.0. 2019.
9. OEKO-TEX®. “STANDARD 100 by OEKO-TEX® test criteria: New regulations in 2020”. OEKO-TEX® Association, Zurich. 2020.
10. Akay DA, Abacı G, Töre GY. “5A3-0642- ASSESMENT OF ECO-CRITERIA IN TERMS OF SUSTAINABILITY APPROACH IN TEXTILE SECTOR” in Proceedings of the 19th World Textile Conference-Autex. 2019; 2019: 5-5.
11. Akter S, Azim AYMA, Faruque MAAI. “Medical textiles: significance and future prospect in Bangladesh”. European Scientific Journal. 2014; 10; 488-502.

12. Alam S, Faruque M, Sarker E, Sowrov K, Alam T, Haque A. “Development of Knitted Gauze Fabric as Wound Dressing for Medical Application”. Adv Res Text Eng. 2018; 3: 1021.

13. Amutha K. “Sustainable chemical management and zero discharges,” in Sustainable Fibres and Textiles. Elsevier. 2017; 347-366.

14. Gomez M, Matafonova G, Gomez J, Batoev V, Christofi N. “Comparison of alternative treatments for 4-chlorophenol removal from aqueous solutions: Use of free and immobilized soybean peroxidase and KrCl excilamp”. Journal of hazardous materials. 2009; 169: 1-3.

15. Flock C, Bassi A, Gijzen M. “Removal of aqueous phenol and 2-chlorophenol with purified soybean peroxidase and raw soybean hulls”. Journal of Chemical Technology & Biotechnology: International Research in Process. Environmental & Clean Technology. 1999; 74: 303-309.

16. Karci A. “Degradation of chlorophenols and alkylphenol ethoxylates, two representative textile chemicals, in water by advanced oxidation processes: the state of the art on transformation products and toxicity”. Chemosphere. 2014; 99: 1-18.

17. Raza W, Lee J, Raza N, Luo Y, Kim KH, Yang J. “Removal of phenolic compounds from industrial waste water based on membrane-based technologies,” Journal of industrial and engineering chemistry. 2019; 71: 1-18.

18. Özbelge TA, Özbelge ÖH, Başkaya SZ. “Removal of phenolic compounds from rubber-textile wastewaters by physico-chemical methods,” Chemical Engineering and Processing: Process Intensification. 2002; 41: 719-730.

19. Van Aken P, Van den Broeck R, Degrève J, Dewil R. “The effect of ozonation on the toxicity and biodegradability of 2, 4-dichlorophenol-containing wastewater,” Chemical Engineering Journal. 2015; 280: 728-736.

20. Chun-Te Lin J, Sopajaree K, Jitjanesuwan T, Lu MC. “Application of visible light on copper-doped titanium dioxide catalyzing degradation of chlorophenols,” Separation and Purification Technology. 2018; 191: 233-243.

21. Karri RR, Jayakumar N, Sahu J. “Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon”. Journal of Molecular Liquids. 2017; 231: 249-262.

22. Wang Z. “Both degradation and AOX accumulation are significantly enhanced in UV/peroxymonosulfate/4-chlorophenol/Cl- system: two sides of the same coin?”. RSC advances. 2017; 7: 12318-12321.

23. Cherubini F. “The biorefinery concept: using biomass instead of oil for producing energy and chemicals”. Energy conversion and management. 2010; 51: 1412-1421.