# REMOVAL OF ACID RED FROM AQUEOUS MEDIUM BY USING ACTIVATED CARBON FROM ACRYLIC WASTE

NAEEM Muhammad Salman[1], GILANI Syed Qummer Zia[1], WIENER Jakub[1], MILITKY Jiri[1], BAHETI Vijay[1], JAVED Saima[2]

[1]*Faculty of Textile engineering, Department of Material engineering, Technical university of Liberec, Czech Republic, EU*

[2]*Department of Microbiology and molecular genetics, Punjab University Lahore, Pakistan*
salman.ntu@gmail.com

**Abstract**

In this work, activated carbon (AC) web was prepared by using waste acrylic fibers followed by physical activation under the layer of charcoal in high temperature furnace. The carbonization of acrylic fibrous waste was performed at different temperature (800, 1000 and 1200 °C) with heating rate of 300 °Chr$^{-1}$ and at different holding time. At 1200 °C the heating rate of 300 °Chr$^{-1}$ with no holding time provided better results of surface area as compared to carbonization at 800 °C and 1000 °C. The AC web prepared at 1200 °C was used for removal of Acid Red 27 dye from aqueous media by varying different parameters like initial concentration of dye, stirring speed, adsorbent dosageand at different levels of pH.

**Keywords:** Physical activation, stabilization carbonization, heating rate, holding time, activated carbon

## 1. INTRODUCTION

Rapid industrialization due to development in the field of science and technology with huge burden of population is causing a severe threat to environment. One of the most important sources of pollution these days is excessive use of dyes. The use of dyes is increasing day by day due to increased demand in leather, tanning, paper production and textile industries. Dyes are used to give colors and currently more than 10.000 dyes with a production of 1 million tons under different trade names are used [1]. Acid red 27 is anionic dye used to color synthetic and natural fibers. But this dye has been banned in many countries due to suspected carcinogenic, however it is still used in many countries. The use of synthetic dyes is increasing due to their low cost but their complex structure makes them difficult to degrade causing more difficulty in their removal from waste water effluent [2][3]. Different waste water techniques are being used for removal of wastes like biological, chemical and physical methods. As synthetic dyes have complex aromatic structure structure so they are not removed by biological methods due to their low bio-degradation behavior [4]. Chemical techniques are not only expensive but also results in accumulation of sludge which in turn creates problem of disposal [2]. Physical adsorption is very effective method for the removal of dyes from waste water. In physical adsorption, activated carbon (AC) is widely used as adsorbent material. Around 80% of produced activated carbon is used in liquid phase applications. The additional benefits of adsorption are cost effective, simple and devoid of hazardous material [5][6][7].

Despite the promising developments in textile applications, the increased demands also brought challenges to dispose large amount of wastes generated during their processing. Generally textile wastes are classified as either pre-consumer or post-consumer textile waste. Pre-consumer textile waste is the leftovers or byproducts from textile, fiber-or cotton industries. On the other hand, post-consumer textile wastes are the wastes of textile products such as fleece, flannel, corduroy, cotton, denim, wool, and linen. These wastes are generally discarded as landfills or incinerated as an alternative fuel source. In recent years, research on

recycling and reuse of textile wastes, instead of landfilling or incineration, has gained a lot of importance due to the increased awareness of environmental concerns. This is because, textiles in landfill biodegrade to form methane gas and release it into the air which is not suitable for human consumption. Similarly incineration of textile wastes lead to release of toxic fumes which are hazardous in nature. European Union (EU) typically being more progressive on environmental issues have implemented laws (Directive 2000/53/CE) to prevent the landfilling of waste materials [8][9]. In the context of environment protection and current disposal of the textile wastes, it becomes essential to recover useful products from them for economic reasons. Traditionally, textile wastes are converted into individual fiber stage through cutting, shredding, carding, and other mechanical processes. However, due to increase in competition and reduced profit margins in these industries, it has become important to search for new recycling techniques to utilize them for high end applications.

In this work, acrylic fibrous waste after converting into non-woven web was carbonized to activated carbon web by physical activation in high temperature furnace. Later, the yield %, specific surface area, shrinkage, surface area and elemental analysis of carbonized samples was performed. The study presented the utility of prepared activated carbon web for the removal of acid red 27 dyes from aqueous solution using adsorption kinetics.

## 2. EXPERIMENTAL METHODS

### 2.1. Materials

The acrylic fibrous waste was taken from Grund Industries of Czech Republic in the form of bath mats. These fibers have acrylonitrile copolymer 85-89%. Acid red 27 was purchased from Sigma Aldrich, Czech Republic.

### 2.2. Conversion of acrylic fibrous waste into ac web

The acrylic fibers were separated from bath mats by using mechanical cutting. The fibers were further opened on laboratory roller card (Befama, Poland) and converted into compact structure of non-woven web by using needle punching machine. Initially the acrylic web was stabilized then carbonized at different temperatures and heating rates as shown in **Table 1**.

**Table 1** Carbonization parameters for acrylic fibrous waste

| Sample No. | Final pyrolysis temperature (°C) | Heating rate (°C $hr^{-1}$) |
|---|---|---|
| 1 | 800 | 150 |
| 2 | 800 | 300 |
| 3 | 800 | 450 |
| 4 | 1000 | 150 |
| 5 | 1000 | 300 |
| 6 | 1000 | 450 |
| 7 | 1200 | 150 |
| 8 | 1200 | 300 |
| 9 | 1200 | 450 |

### 2.3. Characterization of prepared AC web

The activated carbon webs prepared at different temperatures were characterized for determining their specific surface, elemental analysis and yield. The yield of activated carbon web was determined by using equation 1.

$$Yield = \frac{Final\ weight\ of\ AC\ web}{Initial\ weight\ of\ acrylic\ web} \times 100 \quad (1)$$

The specific surface area of activated carbon webs was determined by nitrogen adsorption desorption isotherms at 77.3 K using Quantachrome instrument. The isotherms measured were taken in relative pressure P/Po (range from 0.02 to 1). Energy disperse x-ray spectroscopy analysis (EDX) helped to understand the proportion of different elements in AC prepared at different temperatures. The morphology of activated carbon and dye adsorbed activated carbon web was studied by the help of Scanning electron microscope (SEM) at 30 kV accelerated voltage.

### 2.4. Adsorption of acid red 27 on to ac non-woven web

The aqueous solution of acid red with different concentrations was prepared by dissolving the required amount of dye in distilled water in ordere to get different concentrations (5.0, 10.0, 15.0, 20.0 and 25.0 mg $L^{-1}$). The adsorption performance was investigated by using batch method. A constant amount of AC web (i.e. 0.1 g) was introduced in each flask having 50 ml of dye solution and was placed on water bath shaker. UV-visible spectrophotometer (UV-1600 pc spectrophotometer) was used for determining the concentration of dye. The dye removal efficiency was calculated by using equation 2.

$$Dye\ removal\ efficiency = \left[\frac{(C_o - C_e)}{C_o} \times 100\right] \quad (2)$$

Where $C_o$ (mg $L^{-1}$) and $C_e$ (mg $L^{-1}$) are initial and final concentrations of dye before and after the addition of adsorbent (activated carbon web). The adsorption capacity of activated carbon web was calculated from equation 3.

$$Adsorption\ capacity\ (q_e) = (C_o - C_e)\frac{V}{W} \quad (3)$$

Where $q_e$ (mg $g^{-1}$) is the amount of dye adsorbed or accumulated on adsorbent, V is the volume of solution in liters and W is the mass of adsorbent in grams.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Effect of carbonization parameters on the properties of ac web

The physical properties of activated carbon webs prepared at different temperatures (800 °C, 1000 °C and 1200 °C) with different heating rates (150, 300 and 450 °$Chr^{-1}$ ) and no holding time are shown in **Table 2**. Initially the acrylic webs were stabilized at 250 °C with slow heating rate (35°$Chr^{-1}$). Black color after stabilization indicated that web was properly stabilized due to cyclization, dehydrogenation and oxidation of PAN structure [10]. During stabilization nitrile groups assisted in formation of ladder structure which enhanced mechanical properties and yield of final carbon web. During carbonization process, further cross-linking converted stabilized web into turbostratic carbon structure with more orientation of carbon basal planes. The activated carbon web prepared at 800 °C with heating rate 150, 300 and 450 °$Chr^{-1}$ provided surface area of 104, 120 and 90 $m^2g^{-1}$. Similarly at 1000 °C it give 170, 190 and 140 $m^2g^{-1}$. Whereas at 1200 °C, the surface area were 240, 278 and 210 $m^2g^{-1}$ at heating rate of 150, 300 and 450 °$Chr^{-1}$ respectively. Literature also showed almost similar surface area by using physical activation with different precursor materials [11][12].

**Table 2** Effect of carbonization parameters on AC web properties

| Temperature (°C) | Yield (%) | Flexibility | Dusting |
|---|---|---|---|
| Heating rate (150 °C $hr^{-1}$) | | | |
| 800 | 56.62 | Good | Good |
| 1000 | 49.32 | Good | Good |
| 1200 | 37 | Poor | Poor |
| Heating rate (300 °C $hr^{-1}$) | | | |
| 800 | 61.70 | Good | Good |
| 1000 | 57.14 | Average | Average |
| 1200 | 45.33 | Poor | Poor |
| Heating rate (450 °C $hr^{-1}$) | | | |
| 800 | 63.47 | Good | Good |
| 1000 | 61.38 | Poor | Poor |
| 1200 | 51.56 | Poor | Poor |

The increase in surface area at high temperature was due to more reaction of atmospheric oxygen with carbonizing structure, which caused elimination of different elements from structure and rearrangement of basal planes. These two reasons were main driving forces for creation of porous structure as can be seen from **Figure 1**.

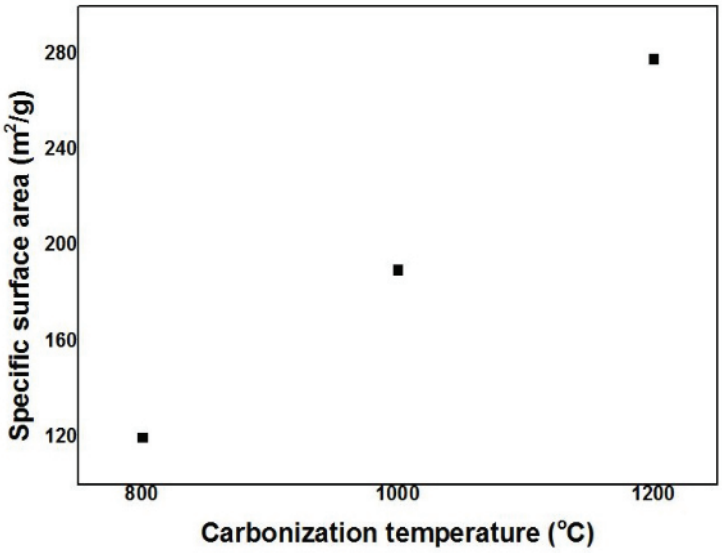


**Figure 1** Effect of carbonization temperature on specific surface area of AC web

### 3.2. Energy disperse x-ray spectroscopy analysis

Energy disperse x-ray spectroscopy analysis (EDX) gave the relative proportion of different elements present in carbon webs prepared at different temperatures (800, 1000 and 1200 °C) with heating rate 300 °C $hr^{-1}$ as can be seen from **Table 3**. It was clear from **Table 3** that by increasing carbonization temperature from 800 °C to 1200 °C the carbon content was increased (CK, which means excitation in K shell), however with reduction in concentration of oxygen (OK, which means excitation in K shell). The AC web produced at 1200 °C showed 92.49 % and 6.61 % content of carbon and oxygen respectively, due to elimination of nitrogen, sulfur, hydrogen and other elements [13].

**Table 3** Effect of carbonization temperature on elemental composition of AC web

| Element | App conc. | Intensity | Weight (%) | Atomic (%) |
|---|---|---|---|---|
| 800 °C | | | | |
| CK | 0.26 | 2.12 | 0.13 | 91.76 |
| OK | 0.01 | 0.76 | 0.01 | 8.24 |
| 1000 °C | | | | |
| CK | 0.37 | 2.12 | 0.18 | 91.87 |
| OK | 0.02 | 0.76 | 0.02 | 8.13 |
| 1200 °C | | | | |
| CK | 0.18 | 2.10 | 0.09 | 92.49 |
| OK | 0.01 | 0.74 | 0.01 | 6.61 |
| CaK | 0.00 | 0.90 | 0.00 | 0.90 |

### 3.3. SEM morphology

For determination of porosity the surface morphology of activated carbon webs prepared at different temperatures was analyzed. **Figure 2 (a-d)** showed the SEM images of pure acrylic and AC webs produced at 800 °C, 1000 and 1200 °C. It was clear from SEM images that as temperature of carbonization increased, roughness of surfaces also increased. The increased in surface roughness indicated the more porous structure at high temperature.

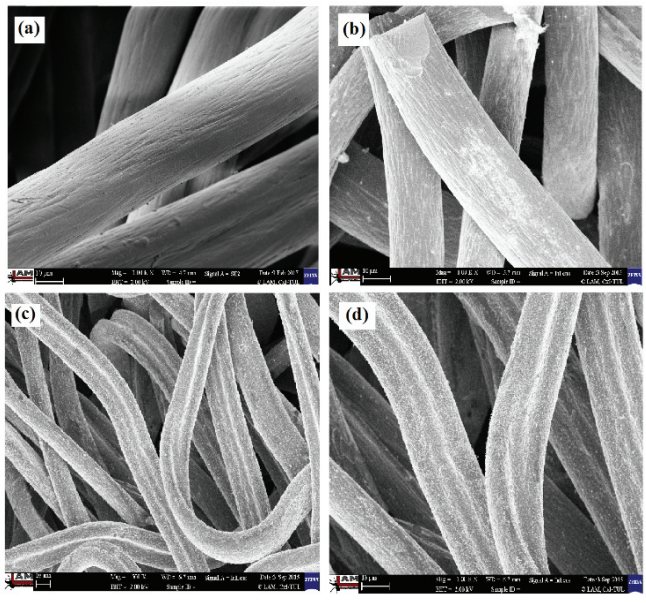


**Figure 2** (a) SEM image of acrylic web, (b) SEM image of AC prepared at 800 °C (c) SEM image of AC prepared at 1000 ° (d) SEM image of AC prepared at 1200 °C

### 3.4. Effect of process parameters on dye removal efficiency

#### 3.4.1. Effect of initial concentration of dye

For the adsorption experiments (effect of initial concentration of dye, adsorbent dosage, stirring speed and pH), the activated carbon web prepared at 1200 °C with heating rate of 300 °Chr$^{-1}$ has been used because of its high surface area. The dye adsorption performance of activated carbon was investigated by varying the

initial concentration of dye from 5 mg $L^{-1}$ to 25 mg $L^{-1}$. It is clear that dye removal percentage increased by increasing contact time and then achieved a constant value when the process reached at equilibrium as can be seen from **Figure 3**. As far as dye removal efficiency was concerned, it decreased from 92.59 % to 76.31 % when the concentration of dye was increased from 5 mg $L^{-1}$ to 25 mg $L^{-1}$ while keeping other factors constant like dosage of activated carbon, stirring speed and temperature.

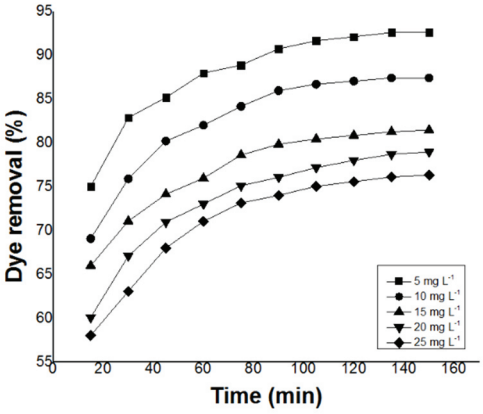


**Figure 3** Effect of initial concentration of dye on removal efficiency

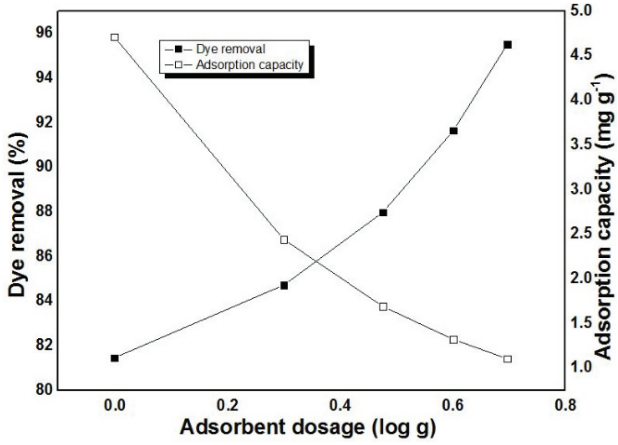


**Figure 4** Effect of adsorbent dosage on dye removal and adsorption capacity

### 3.4.2. Effect of adsorbent dosage

The effect of adsorbent dosage on dye removal efficiency and adsorption capacity was analyzed by changing the adsorbent dosage from 1 mg $L^{-1}$ to 5 mg $L^{-1}$ while keeping other factors same like contact time 150 minutes, temperature 25 °C, 15 mg $L^{-1}$ acid red concentration and a stirring speed of 200 rpm. From **Figure 4**, it was clear that dye removal efficiency increased as the quantity of activated carbon was increased. The acid red removal percentage was 81.46 % when 1 g $L^{-1}$ adsorbent (activated carbon) was used. However this trend of dye removal efficiency kept on increasing to 84.72 %, 87.98 %, 91.64 % and 95.51 % when the quantity of activated carbon was increased to 2 g $L^{-1}$, 3 g $L^{-1}$, 4 g $L^{-1}$ and 5 g $L^{-1}$ respectively. This increase in dye removal efficiency is attributed to increased surface area of adsorbent and more availability of active sites resulting from increased adsorbent dosage. Similar results have been reported by removal of acid dye on granular AC [19,20]. However, there was an inverse trend when the adsorbent dosage and adsorption capacity of activated carbon were analyzed. This is probably due to the reason that adsorption sites present on activated carbon remained unsaturated in adsorption process, hence a fall in adsorption capacity was expected [14].

### 3.4.3. Effect of stirring speed

The effect of stirring speed on dye removal efficiency and adsorption capacity was investigated by keeping acid red concentration 6 mg $L^{-1}$ , temperature 25 °C, adsorbent dosage 2 g $L^{-1}$ and contact time 150 minutes to ensure that equilibrium point was achieved. The stirring speed was changed from 50 rpm to 200 rpm. One sample was used without the stirring speed for comparing the results. From **Figure 5** it was clear that only 2.44 % dye was removed without any stirring. However as the stirring speed was increased dye removal efficiency was found to increase to 30.75 %, 57.23 %, 71.89 % and 81.78 % respectively. As far as adsorption capacity was concerned it also increased as the stirring speed was increased. The adsorption capacity of activated carbon increased from 1.78 mg $g^{-1}$ to 3.31 mg $g^{-1}$, 4.155 mg $g^{-1}$ and 4.71 mg $g^{-1}$ when the stirring speed was increased from 50 rpm to 100 rpm, 150 rpm and 200 rpm respectively. This trend is obvious due to more interaction of dye solution with the adsorbent at high stirring speed [15].

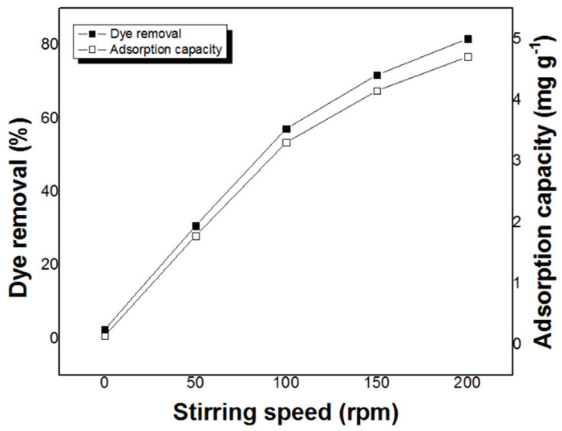


**Figure 5** Effect of stirring speed on dye removal and adsorption capacity

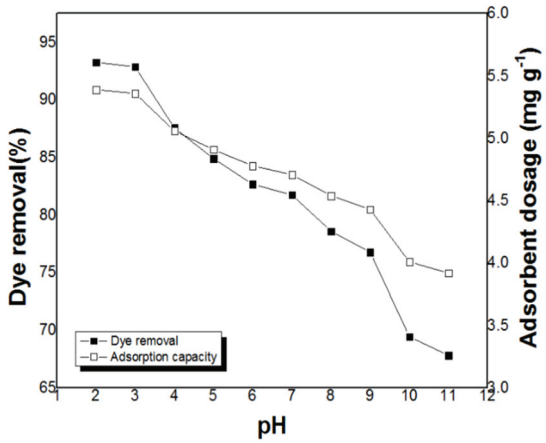


**Figure 6** Effect of pH on dye removal efficiency and adsorption capacity

### 3.4.4. Effect of pH

The pH of solution has significant effect on the dye removal efficiency and adsorption performance of activated carbon. For analyzing dye removal efficiency of acid red, pH of solution was varied from 2 to 11, while keeping other parameters constant like adsorbent dosage 2 mg $L^{-1}$, dye concentration 15 mg $L^{-1}$, stirring speed of 200 rpm temperature 25°C and contact time 150 minutes to ensure that equilibrium was achieved. The point of zero charge of AC web prepared by pyrolysis of acrylic fibrous waste was found to be 5.90. It is the point at which the net charge on the surface of activated carbon is zero [16]. At pH > $pH_{ZPC}$ the surface of adsorbent is negatively charged while at pH < $pH_{ZPC}$ the surface becomes positively charged [17][18]. The pH of solution was varied by the help of sodium hydroxide (NaOH) and hydrochloric acid (HCL). It is clear from **Figure 6** that maximum dye removal efficiency (93.27%) was observed at pH 2, while minimum dye removal (67.82%) was observed at pH 11.

At pH value lower than the point of zero charge of activated carbon the surface of activated carbon becomes positively charged due to accumulation of positive ions ($H^+$). Therefore, as the pH value was reduced, the adsorption capacity and dye removal efficiency was increased due to electrostatic attraction between positively charged activated carbon and anionic dye molecules ($AR^-$). This force of attraction is mainly responsible for the removal of dye molecules from the solution. However as the pH of solution was increased further, the dye removal efficiency and adsorption capacity decreased due to accumulation of negatively charge on the surface of adsorbent. This force of repulsion between anionic dye molecules and surface of activated carbon was mainly responsible for less removal of dye at high pH. Similar results have been reported by Shah and coworkers [19] where they found that electrostatic force of attraction and repulsion played significant effect in dye removal from solution.

## 4. CONCLUSION

The acrylic fibrous waste was successfully converted into activated carbon web by physical activation at different temperatures (800°C, 1000 °C and 1200 °C) with different heating rates of 150, 300 and 450 °C $hr^{-1}$ with no holding time under the layer of charcoal. The higher surface area 278 $m^2/g$ was achieved at higher temperature 1200 °C with 300 °C $hr^{-1}$ due to more elimination of different elements from carbonized material and due to mutual arrangement of carbon sheets. Later the adsorption performance of acid red on activated carbon was examined by varying different parameters like varying the initial concentration of dye from 5 mg $L^{-1}$ to 25 mg $L^{-1}$, adsorbent dosage, stirring speed and different pH of solutions. From the results, it was clear that more equilibrium time was required when the concentration of dye was increased. However, when the adsorbent dosage and stirring speed was increased, it took less time to remove dye.

## ACKNOWLEDGEMENTS

***This work was supported under the student grant scheme (SGS-21198) by Technical University of Liberec, Czech Republic.***

## REFERENCES

[1] V. K. GUPTA and SUHAS, "Application of low-cost adsorbents for dye removal-A review," *J. Environ. Manag*, vol. 90, no. 8, pp. 2313-2342, 2009.

[2] C. . HUANG, K. . CHANG, H. . OU, Y. . CHIANG, and C. . WANG, "Adsorption of cationic dyes onto mesoporous silica," *Microporous Mesoporous Mate*, vol. 141, no. 1, pp. 102-109, 2011.

[3] E. FORGACS, T. CSERHÁTI, and G. OROS, "Removal of synthetic dyes from wastewaters: a review," *Env. Int*, vol. 30, no. 7, pp. 953-971, 2004.

[4] G. CIARDELLI and N. RANIERI, "The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation," *Water Res*, vol. 35, pp. 567-572, 2001.

[5] R. C. BANSAL, *Activated Carbon Adsorption*, 1st ed. London, U.K: Taylor and Francis Group, 2005.

[6] H. RICHARD, *Recycling textile and plastic waste*, 1st ed. London, UK: Woodhead publishing, 1996.

[7] P. SORAIA and T. SILVESTRE, "Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook," *Waste Manag*, vol. 31, pp. 378-392, 2011.

[8] E. SANO and E. AKIBA, "Electromagnetic absorbing materials using nonwoven fabrics coated with multi-walled carbon nanotubes," *Carbon N. Y*, vol. 78, pp. 463-468, 2014.

[9] M. CAO, X. WANG, W. CAO, and J. YUAN, "Ultrathin graphene: electrical properties and highly efficient electromagnetic interference shielding," *J. Mater. Chem.*, vol. 26, no. 3, pp. 14-21, 2015.

[10] P. CHAE, GULGUNJE, and S. KUMAR, "Y. LIU, Y. H. CHOI, H. G. Temperature dependent tensile behavior of gel-spun polyacrylonitrile and polyacrylonitrile/carbon nanotube composite fibers," *Polym. Guildf*, vol. 54, no. 2, pp. 4003-4009, 2013.

[11] M. . ZAINI, Y. AMANO, and M. MACHIDAA, "Adsorption of heavy metals onto activated carbons derived from polyacrylonitrile fiber," *J. Hazard. Mater*, vol. 180, pp. 552-560, 2010.

[12] S. JAGANNATHAN, H. . CHAE, and R. JAIN, "Structure and electrochemical properties of activated polyacrylonitrile based carbon fibers containing carbon nanotubes," *J Power Sources*, vol. 185, pp. 676-684, 2008.

[13] S. NAEEM, V. BAHETI, V. TUNAKOVA, J. MILITKY, K. DANIEL, and B. TOMKOVA, "Development of porous and electrically conductive activated carbon web for effective EMI shielding applications," *Carbon N. Y*, vol. 111, pp. 439-477, 2017.

[14] S. MARIUS, C. BENOIT, C. IGOR, D. MARIANA, and P. STELIAN, "Removal of an Acid Dye from Aqueous Solution by Adsorption on a Commercial Granular Activated Carbon:Equilibrium, Kinetic and Thermodynamic Study," *Sci. Study Res*, vol. 12, no. 4, pp. 307-322, 2011.

[15] S. NAEEM, V. BAHETI, J. MILITKY, J. WIENER, P. BEHERA, and A. ASHRAF, "Sorption properties of iron impregnated activated carbon web for removal of methylene blue from aqueous media," *Fibers Polym*, vol. 17, pp. 1245-1252, 2016.

[16] M. A. RAHMAN, S. M. R. AMIN, and A. M. S. ALAM, "No Title," *Dhaka Univ. J. Sci.*, vol. 60, pp. 185-191, 2012.

[17] Y. AL-DEGS, M. . EL-BARGHOUTHI, A. EL-SHEIKH, and G. . WALKER, "Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon," *Dye. Pigment*, vol. 77, pp. 16-23, 2008.

[18] Y. AL-DEGS, M. KHRAISHEH, S. ALLEN, and M. AHMAD, "Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent," *Water Res*, vol. 34, no. 3, pp. 927-935, 2000.

[19] I. SHAH, R. ADNAN, W. NGAH, and Y. TAUFIQ, "Iron impregnated activated carbon as an efficient adsorbent for the removal of methylene blue: regeneration and kinetics studies," *PLoS One, vol. 10, 2015*, vol. 10, no. 4, 2015.