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DEVELOPMENT OF ACTIVATED CARBON WEB FROM ACRYLIC FIBROUS WASTE

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SUMMARY OF THE THESIS

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Abstract

Activated carbon fibers have gained significant attention since the last decade due to their extra-ordinary adsorption characteristics towards heavy metals, different poisonous gases, dyes and other hazardous chemicals. Besides high adsorption capacity, the thermal and electrical conductive properties of activated carbon fibers are driving forces towards thermal, electrical and electromagnetic shielding applications. Different precursors used for formation of activated carbon fibers are cellulosic based, polyacrylonitrile, pitch based, polyimides, phenolic resins and polyethylene based materials. However, researchers are inquest to find out different precursor materials and methods for reducing the cost of activated carbon fibers. In this context, use of acrylic fibrous waste together with a novel method of single stage carbonization and activation by using physical activation under the layer of charcoal was explored in this study.

For converting precursor material into activated carbon fiber, firstly the material was stabilized then carbonized at high temperature. Heating rate, holding time and final pyrolysis temperature played very important role in getting good values of electrical conductivity (surface and volume conductivity), better electromagnetic shielding effectiveness (ESE) and surface area. In this work optimization of parameters for getting higher surface area and electrical conductivity has been achieved by varying number of steps, holding time (0, 30 and 60 minutes), heating rate (150, 300 and 450 $^{\circ}C\ hr^{-1}$) and final pyrolysis temperature (800, 1000 and 1200 $^{\circ}C$). It was found that heating rate 300 $^{\circ}C\ hr^{-1}$, holding time zero minute, final pyrolysis temperature 1200 $^{\circ}C$ with two step approach were the optimized parameters for getting good surface area and electrical conductivity. Later the waste of acrylic fibers was converted into a compact structure of non-woven web by using roller carding and needle punching machine. The non-woven web was transferred to high temperature furnace for stabilization and carbonization on parameters finalized. The yield and shrinkage of activated carbon webs prepared at different temperatures were determined by measuring weight and change in dimensions before and after carbonization respectively. Likewise the flexibility or stiffness and dusting properties of activated carbon webs was measured by following the principle of cantilever bending and by rubbing the web on taber wear and tester. The surface morphology and chemical characterization of activated carbon webs was done by using Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Brunauer emmett teller (BET).

The electrical conductivity and electromagnetic shielding effectiveness of AC webs was determined by using parallel electrode and concentric electrode and by using wave guide method and coaxial transmission line method. It showed that due to more orientation of chains, crystallinity, compactness of chains and higher crystalline content at higher temperature, the web prepared at high temperature gave better results of electrical conductivity and shielding effectiveness. The adsorption performance of AC web as well as iron impregnated AC web was checked by using methylene blue at different parameters like different concentrations of dye, adsorbent dosage, stirring speed and pH. Later the results were verified by using adsorption isotherms (Freundlich and Langmuir) and kinetics (pseudo 1^{st} and 2^{nd} order) of reaction. It was found that metal impregnation increased surface area hence more adsorption of dye molecules.

Key words: Acrylic, activated carbon, stabilization, carbonization, graphitization, adsorption

Abstrakt

Aktivní uhlíková vlákna získala značnou pozornost v posledních desetiletích v důsledku mimořádných adsorpčních vlastností vůči těžkým kovům, toxickým plynům, barvivům a dalším nebezpečným chemikáliím. Vedle vysoké adsorpční kapacity jsou hnací sílou vývoje aktivních uhlíkatých vláken také aplikace proti tepelnému, elektrickému a elektromagnetickému stínění. Různé prekurzory používané pro přípravu těchto vláken jsou na celulózové bázi, bázi polyakrylonitrilu, dehtu, polyimidu, fenolových pryskyřic a polyetylenu. Výzkumní pracovníci se věnují hledání různých materiálů a metod pro snížení nákladů na aktivní uhlíková vlákna. V této práci je využíván odpad akrylových vláken společně s novou metodou jednostupňové karbonizace a fyzikální aktivace pod vrstvou dřevěného uhlí.

Pro přeměnu vstupního materiálu na aktivní uhlíkové vlákno je vstupní materiál stabilizován a následně karbonizován při vysoké teplotě. Rychlost ohřevu, čas prodlevy a konečná teplota pyrolýzy hrají významnou roli v získání požadovaných hodnot elektrické vodivosti (povrchová a objemová vodivost), lepší účinnosti elektromagnetického stínění (ESE) a relativní plochy povrchu. Tato pracovní optimalizace parametrů pro získání větší plochy povrchu a elektrické vodivosti byla realizována s měnícím se počtem kroků, časy prodlevy (0, 30 a 60 minut), rychlostmi ohřevu (150, 300 a 400 °C/hod) a konečnými teplotami pyrolýzy (800, 1000 a 1200 °C). Bylo zjištěno, že rychlost ohřevu 300 °C/hod, čas prodlevy 0 minut a finální teplota pyrolýzy 1200 °C s dvoufázovým postupem jsou optimální parametry pro získání dobré plochy povrchu a elektrické vodivosti. Později byl odpad z akrylových vláken přeměněn na kompaktní struktury netkaných pásů pomocí mykání a vpichováním. Netkané pásy byly převedeny vysokými teplotami pece po stabilizaci a karbonizaci na finální parametry. Výtěžek a smrštění aktivních uhlíkových pásů při různých teplotách byl zjišťován pomocí měření hmotnosti před a po karbonizaci a změny rozměrů byly zjišťovány rovněž před a po karbonizaci. Podobně flexibilita nebo tuhost a prášivost aktivních uhlíkových pásů byly měřeny podle principů měření Cantilever testem a odíráním pásů proti opotřebí Taber Wear and Abrasion Testerem. Povrchová morfologie a chemická struktura aktivních uhlíkových pásů byla měřena pomocí rastrovacího elektronového mikroskopu (SEM), energetické disperzní rentgenové mikroskopie (EDX), rentgenové difrakce (XRD) a metodou izotermy Brunauer-Emmet-Teller (BET).

Elektrická vodivost a účinnost elektromagnetického stínění aktivních uhlíkových pásů byla stanovena pomocí paralelní a soustředné elektrody a pomocí metody "coaxial transmission line". Ukázalo se, že v důsledku vyšší orientace řetězců, kompaktnosti řetězců a vyššímu obsahu krystalinity při vyšší teplotě pás připravený při vysoké teplotě dává lepší výsledky elektrické vodivosti a účinnosti stínění. Adsorpční schopnosti aktivních uhlíkových pásů stejně jako železem impregnovaných aktivních uhlíkových pásů byly stanoveny adsorpcí použitím metylenové modři při různých parametrech jako například různé koncentrace barviva, adsorpční dávce, rychlosti míchání či pH. Výsledky byly ověřeny pomocí adsorpčních izoterm (Freundlichova a Langmuirova) a reakční kinetiky (pseudo-prvního a druhého řádu).

Klíčová slova: akrylový, aktivní uhlík, stabilizace, karbonizace, grafitizace, adsorpce

SUMMARY

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1. Introduction

Nowadays electrically conductive textiles are of great interest due to numerous applications in various fields like military and medical fields, as actuators and sensors and for electromagnetic shields etc. Electrically conductive fabrics can be obtained through different means like metallization, chemical coating, deposition of thin layers of conductive fillers like carbon black particles or through the insertion of metallic yarn [1]. Most of the synthetic fibers used in textiles are insulating materials with resistivity around 10^{15} Ω/cm^2. This resistivity is much higher than the desired for anti-electrostatic and electromagnetic shielding applications. The desired resistivity for electromagnetic shielding materials should be lower than 10^2 Ω/cm^2 and for anti-electrostatic materials it should be in the range of 10^9-10^{13} Ω/cm^2 [2]. Conductive fibers are classified as naturally conductive and those that are specially treated to make conductive. Natural conductive fibers are carbon fibers or fibers developed from inherently conductive polymers or metallic fibers [3, 4].

In recent years, research on electromagnetic interference (EMI) shielding materials has attracted significant attention due to increase in electromagnetic population from widespread applications of computers and telecommunication technologies [5, 6]. The emitted electromagnetic radiations are of concern since they interfere with the working of other appliances as well as cause serious health risks to humans [7]. The EMI shielding effectiveness of material is governed by reflection, absorption and multiple internal reflections of incident electromagnetic radiations [8, 9]. Reflection is commonly used shielding mechanism by high electrically conductive materials such as metals and their nanoparticles. Likewise high density, lack of flexibility, easy corrosion, costly processing and weak microwave absorption make them unsuitable to be used for Emi shielding applications [10], however carbon nanostructures and graphene are reported as promising alternatives to metal-based shielding materials [11]. For instance, carbon-based shielding foams are considered predominant in effective shielding mechanism due to their light weight and the synergetic effect of electrical conductivity and multiple reflections. The addition of high concentration of electrically conductive nano-fillers was found to cause undesirable effects on the polymers for formation of porous structure[12]. Therefore, the numbers of studies in recent years focused on the development of lightweight EMI shielding materials using various new approaches. Yan et al. proposed a combination of high-pressure compression molding plus

salt-leaching method to fabricate porous graphene/polystyrene composites. In addition, the chemical vapor deposition and self-assembly of highly aligned graphene sheets into 3D graphene porous structures was found to be efficient in improving the EMI shielding properties [13, 14].

In recent years, quality of fresh air surrounding the living place has gained impotence as it affects health, comfort, satisfaction and productivity of people. In fact, the indoor quality of air is more important than the outdoor air since most people spend an average of 90% of their time in enclosed buildings. The volatile organic compounds are regarded as major source of indoor air contaminants. The few examples of volatile organic compounds are formaldehyde, benzene, toluene, acrolein, radon, ozone, and fine particles, which can be found in cooking or tobacco smoke [6]. A long-term exposure to these compounds causes headaches, dizziness, nausea, or allergic reaction [15]. Likewise the wastewater treatment is a very serious problem in industries of textile, paper production, food technology, tanning and leather, since major portion of this water is polluted by the presence of toxic dyes. Dyes are natural or synthetic aromatic organic compounds used to add or change the color of material. The removal of dyes from textile effluent depends on solubility of dyes, their percentage in wastewater and chemical structure [16]. There is a significant amount of research carried out in past on activated carbon-based adsorbents for removal of heavy metals and dyes from wastewater. Activated carbon is a highly porous product, usually derived from carbon sources such as bituminous coal, lignite, wood, or coconut shell. Activated carbons have a very high porous structure with a large internal specific surface area around 500–2000 m^2 g^{-1} and having good adsorption capacities. Different researchers have tried different methods to modify the structure of activated carbon with iron or other metal oxides. Some researchers used granular activated carbon and mixing it with iron chloride to get iron impregnated activated carbon. In another study activated carbon was stirred with $KMnO_4$ solution for 20 minutes. After separating activated carbon from $KMnO_4$ solution, the residual AC was mixed with iron sulfate to get FeAC.

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 [17, 18]. 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 [19, 20].

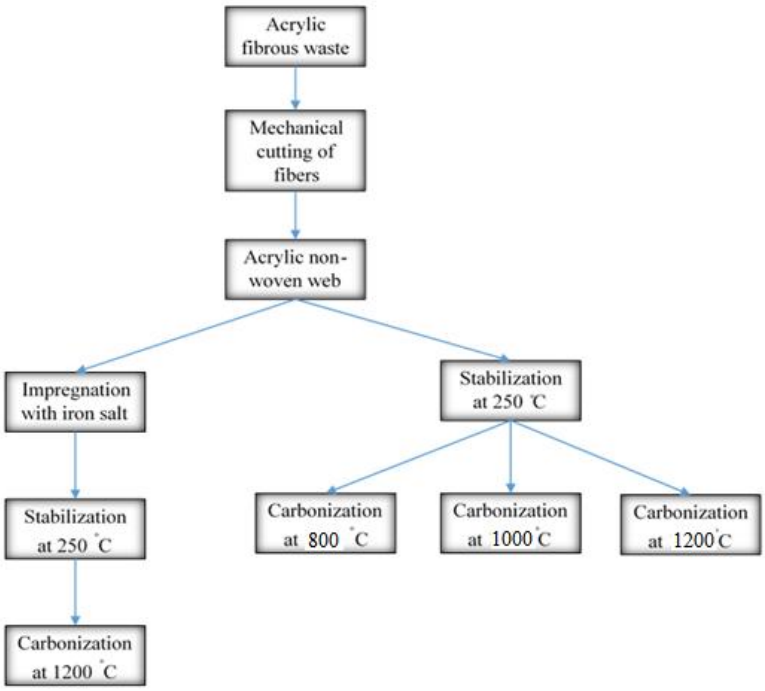

Figure 1. Flow diagram for the formation of AC web and metal impregnated AC web

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 [17, 18]. 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 [20, 21]. In this work acrylic fibrous waste is used as raw material for the formation of activated carbon. Figure 1 gives the flow diagram for the

conversion of acrylic fibrous waste into activated carbon web and for metal impregnation of activated carbon. In Europe where on average one person discards 30 kg of textile waste every year and with a population of more than 500 million for the 27 countries of EU, this equates to approximately more than 18.3 million tons of clothing and textile waste generated every year. The main categories of clothing and textile waste are composed of synthetic materials such as acrylic, nylon and polyester and natural fibers such as wool, flax and cotton [22]. Although textiles can be 100% recyclable but even for the developed countries like America this ratio is as low as 15%. It is reported that the textile that goes to landfilled comprises 80% on synthetic fibers, however the remaining are natural fibers. The natural fibers decompose with the passage of time but synthetic fibers do not. However, practically natural fibers hardly decompose and during decomposition release biogases and toxic leachate [23].

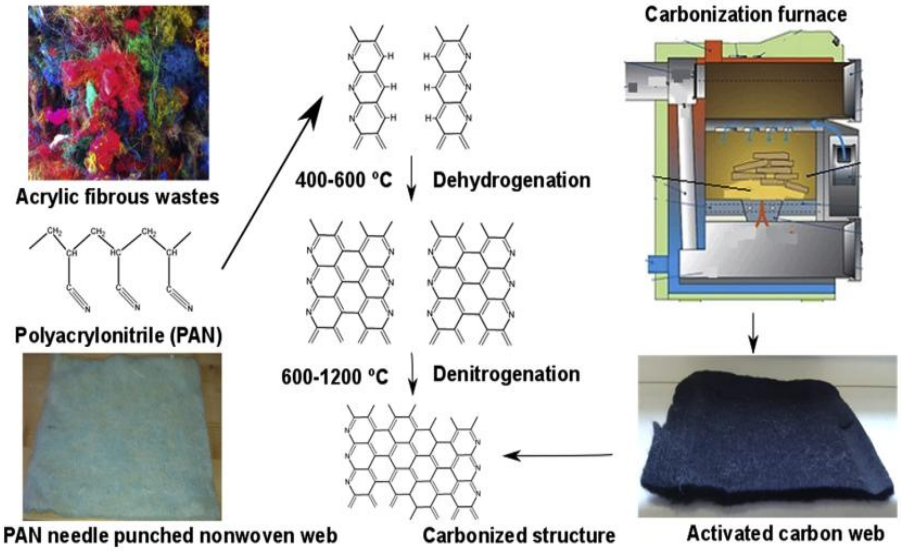

Figure 2. Schematic diagram for the conversion of acrylic fibrous waste into AC web

Hence, in this context the idea of converting acrylic fibrous wastes generated in textile industries into activated carbon is considered as one of the favorable approach. The schematic diagram for the formation of activated carbon web from acrylic fibrous waste can be seen from figure 2. The short acrylic fiber wastes are suitable for porous activated carbon because of their excellent natural structure and low ash content.

The use of acrylic fibrous waste together with a novel method of single stage carbonization and activation by using physical activation under the layer of charcoal has been explored and investigated in this study.

2. Research objectives

The objectives of this study are:

a) To optimize parameters for preparation of activated carbon fibers from acrylic fibrous waste

The objective is to convert acrylic fibrous waste into activated carbon fibres. The main focus is to optimize parameters for the preparation of activated carbon fibers for getting higher values of electrical conductivity and surface area. Different parameters like final pyrolysis temperature (FPT), holding time at final temperature (HTFT), heating rate per hour (HRPH) and Number of steps (NOS) significantly affect functional characteristics like conductivity and surface area. The objective is to find optimum settings for these parameters in order to get higher values of conductivity and surface area.

b) To prepare porous and electrically conductive activated carbon web for better surface area and physical properties

The second objective is to convert needle punched non-woven web into activated carbon web by using carbonization and simultaneously activation for getting better values of surface area, conductivity and physical characteristics. The objective is to get higher values of surface and volume conductivity, surface area, flexibility, dusting, shrinkage and dusting properties of activated carbon webs.

c) Electromagnetic shielding application of activated carbon

For eco-friendly advancements in EMI shielding effectiveness, the development of new light weight shielding materials having strong absorption and weak secondary reflection is necessary. This can be achieved by porous morphology, large specific surface area and higher electrical conductivity of shielding materials. Although number of research studies focused on development of porous carbon based EMI shielding materials, the construction of lightweight structures with excellent EMI shielding properties by simple and cheap method is

still a big challenge. The objective of this work is to prepare simple and novel method for preparation of porous and electrically conductive activated carbon nonwoven web from acrylic fibrous wastes. Another objective is to study better electromagnetic shielding effectiveness of activated carbon webs by increasing thickness of webs.

d) Sorption properties of activated carbon and iron impregnated activated carbon web

The objective is to make the porous structure of activated carbon web by using acrylic fibrous waste. In subsequent stage, the AC web is to use as adsorbent for removal of methylene blue dye from aqueous media. Second part of this study is the surface modification of activated carbon to enhance its adsorption capacity towards cationic dye stuff. As adsorption is a surface phenomenon, so the surface of activated carbon was modified with iron. Most of the researchers have modified surface of activate carbon after making of activated carbon. The objective in this study is to modify surface of activated carbon before stabilization and carbonization.

3. Overview of the current state of problem

The researchers are trying to use alternate inexpensive materials to reduce the cost of activated carbon either by using physical or chemical methods. Amongst different approaches to reduce the cost of activated carbon is to use cheap, alternate and inexpensive materials. It is found that textile waste is a good choice to form and reduce the cost of activated carbon. Millions of tons of textile waste is being landfilled every year. Textile waste is considered as one of the fastest growing sectors in terms of household waste and the amount of waste is forecast to continue growing as sales of new textiles and clothing continue to increase [23]. Hence, in this context the idea of converting acrylic fibrous wastes generated in textile industries into activated carbon is one of the favorable approaches.

For eco-friendly advancements in EMI shielding effectiveness, the development of new light weight shielding materials having strong absorption and weak secondary reflection is necessary. This can be achieved by porous morphology, large specific surface area and higher electrical conductivity of shielding materials. As a result, many lightweight polymer foams with graphene, CNTs, or carbon nano-fibers were produced. Nevertheless, the addition of high concentration of electrically conductive nano-fillers was found to cause undesirable effects on the polymers for

formation of porous structure [12]. Therefore, the numbers of studies in recent years focused on the development of lightweight EMI shielding materials using various new approaches. This work presented the simple and novel method for preparation of porous and electrically conductive activated carbon nonwoven web from acrylic fibrous wastes. The prepared activated carbon is advantageous over carbon made from other materials because of low cost, high density, better purity, and virtually dust-free nature of acrylic fiber.

Since from the last decade, activated carbon fibers are of special attention due to high adsorption capacities and diversity of synthesis in different forms with wider applicability. But now researchers are trying to shift the focus of conventional adsorption characteristics of activated carbon by impregnating it with different chemicals in order to get desired results not only to improve adsorption characteristics but also to incorporate additional characteristics like increasing surface area, anti-bacterial applications and magnetic activated carbon particles for easily removing waste water after adsorption. In this work impact of metal impregnation before stabilization and carbonization has been analyzed for change in porosity and dye removal efficiency.

4 Methods used and material studied

4.1 Material

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%. The physical characteristics of acrylic fibers as shown in table 1.

Table 1. Physical properties of acrylic fibers

Fineness [tex]	117
Tenacity [cN/tex]	23.84
Elongation [%]	45
Wet Shrinkage [%]	2.5

4.2 Methodology

The main objective is to convert acrylic fibrous waste into activated carbon fibers for getting higher surface area and electrical conductivity by optimization of parameters for temperature, heating rate, holding time and number of steps.

4.3 Stabilization and carbonization of acrylic fibrous wastes

The acrylic fibers were first stabilized at 250 $^{\circ}$C at the heating rate of 50 $^{\circ}$C h^{-1}. The stabilized fibers were then pyrolysis under the layer of charcoal in order to have gradual reaction of atmospheric air with carbonized acrylic fibrous waste. The carbonization behavior was studied under four variables: final pyrolysis temperature (FPT), holding time at final temperature (HTFT), heating rate per hour (HRPH) and Number of steps (NOS). The optimization was performed using Box-Behnken design and response surface modeling under three levels and four factors as mentioned in table 2.

Table 2. Selected factors and levels for pyrolysis of acrylic fibrous wastes

Number of factors	Levels		
	[-]	[0]	[+]
FPT ($^{\circ}$C)	800	1000	1200
HTFT (min)	0	30	60
HRPH ($^{\circ}$C hr^{-1})	150	300	450
NOS	1	2	3

4.3.1 Optimization of pyrolysis parameters

Using the Box–Behnken experimental design, twenty seven runs with appropriate combinations of FPT, HTFT, HRPH and NOS were conducted. The results for specific surface area and surface resistivity are given in table 3. The surface area was measured from N_2 adsorption–desorption isotherms at 77.35 K using Quantachrome Instruments. Adsorption/desorption isotherm measurements were collected in the relative pressure range P/P_0 from 0.02 to 1. However for determining Hewlett Packard 4339 B high resistance meter was used. The environmental condition for the measurement was kept at 22 $^{\circ}$C temperature and 40 % relative humidity and voltage used was 100 V.

Table 3. Box-Behnken design showing obtained properties of activated carbon

Run	Final pyrolysis temperature [°C]	Holding time at final temperature [min]	Heating rate [°C hr^{-1}]	Number of steps	BET surface area [m^2 g^{-1}]	Resistivity [Ohm.mm]
1	1200	0	300	2	278	0.52
2	1000	30	450	1	92	130.50
3	1200	30	450	2	90	0.65
4	1000	0	300	3	160	7.83
5	800	0	300	2	120	1174.50
6	1200	60	300	2	213	0.31
7	1000	60	300	1	59	83.52
8	1000	30	300	2	170	28.71
9	1200	30	300	1	58	135.72
10	1000	30	300	2	140	2.47
11	1200	30	150	2	256	0.67
12	800	60	300	2	88	208.80
13	1200	30	300	3	340	0.46
14	800	30	300	1	45	112.23
15	800	30	450	2	63	323.11
16	1000	30	150	1	82	125.28
17	1000	0	150	2	176	4.69
18	1000	60	450	2	135	2.08
19	800	30	150	2	105	169.65
20	800	30	300	3	74	522.00
21	1000	30	150	3	190	6.78
22	1000	60	300	3	179	3.39
23	1000	0	300	1	53	92.92
24	1000	30	300	2	143	3.21
25	1000	60	150	2	121	1.57
26	1000	30	450	3	110	2.35
27	1000	0	450	2	137	3.92

For the estimation of significance of the model, the analysis of variance and the F-test were carried out. The corresponding variables would be more significant when the absolute F-value becomes greater and the p-value (significance probability value) becomes smaller. Using 1.0 % significance level, a model is considered highly significant if the p-value is less than 0.01. From the p-value presented in table 4 and 5, it can be concluded that only the linear contributions in case of specific surface area are highly significant. The square contributions and the interaction contributions are not significant in both cases of specific surface area and surface resistivity. The

coefficient of determination is found to be 94.0 % for specific surface area model and 86.0 % for surface resistivity model, which means that the model could explain 94.0 % and 86.0 % of the total variations in the system.

Table 4. Estimation of significance of model for specific surface area

Source	DF	SS	MS	F-value	p-value
Regression	14	122203.15	8728.79	6.62	0.000
Linear	4	91412.16	22853.04	17.34	0.000
Quadratic	4	7903.00	1975.74	1.49	0.026
Interaction	6	22888.00	3814.66	2.89	0.05
Residual error	12	15814.91	1317.91		
Lack of fit	10	15268.91	1526.89	5.59	0.16
Pure error	2	546.00	273.00		
Total error	26	138018.07			

Table 5. Estimation of significance of model for surface resistivity

Source	DF	SS	MS	F-value	p-value
Regression	14	1143892.28	81706.59	2.46	0.06
Linear	4	553200.37	138300.09	4.16	0.02
Quadratic	4	277465.86	69366.46	2.09	0.14
Interaction	6	313226.03	52204.33	1.57	0.23
Residual error	12	398187.31	33182.27		
Lack of fit	10	397740.87	39774.08	178.18	0.00
Pure error	2	446.44	223.22		
Total error	26	1542079.59			

With the help of canonical analysis in SYSTAT software, set of optimised parameters for both specific surface area and surface resistivity are calculated and given in table 6.

Table 6. Optimum values of pyrolysis parameters

Pyrolysis factor	Specific surface area [m^2/g]	Surface resistivity [Ω.mm]
FPT [^oC]	769.63	970.05
HTFT [min]	17.19	58.40
HRPH [^oC/hr]	382.27	337.52
NOS	1.47	1.72

The three dimensional plots of response surface model are studied for the interaction effect of pyrolysis factors on specific surface area and surface resistivity. The plots are shown from figure 3 to figure 8. The development of porous morphology having higher surface area is found to

increase with increase in pyrolysis temperature, increase in number of steps, decrease in holding time and decrease in heating rate till some optimum value. This behavior is attributed to gradual reaction of atmospheric oxygen with carbonized acrylic fibrous waste, which resulted into the opening of previously inaccessible pores through the removal of tars and disorganized carbon [24]. Moreover, these four factors also found to have significant effect on the development of electrical conductivity than surface area of activated carbon. It is clear from figure 6 (a) & (b) that the effect of heating rate was more pronounced for increased specific surface area than the effect of holding time. The slower heating rate below 300 $^{\circ}C\ hr^{-1}$ was found more advantageous for gradual increase in reactivity between atmospheric oxygen and carbon. However, with increase in holding time, the chances of sudden increase in reactivity between atmospheric oxygen and carbon are higher. As a result, the reduction in values of specific surface area with increase in holding time can be observed.

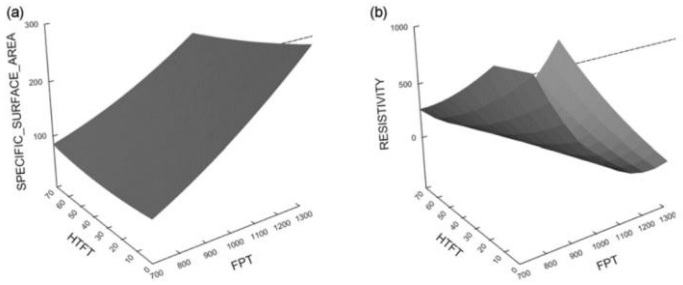

Figure 3. Effect of (a) FPT and HTFT on specific surface area and (b) FPT and HTFT on surface resistivity

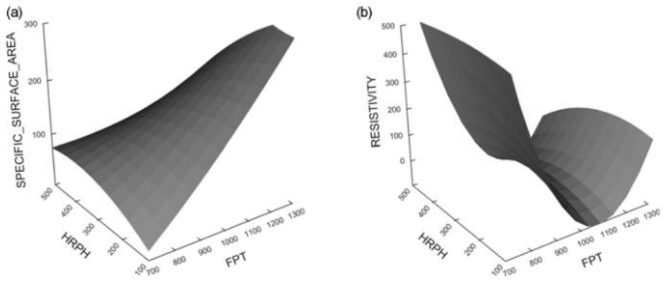

Figure 4.Effect of (a) FPT and HRPH on specific surface area and (b) FPT and HRPH on surface resistivity

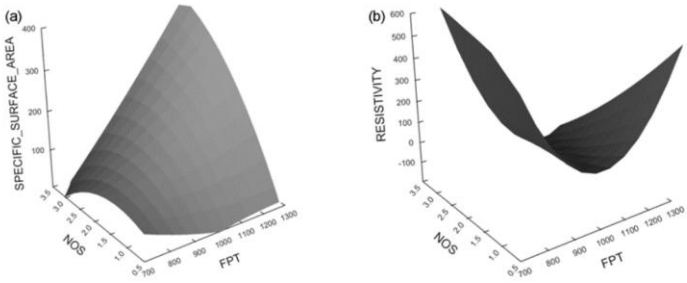

Figure 5. Effect of (a) FPT and NOS on specific surface area and (b) FPT and NOS on surface resistivity

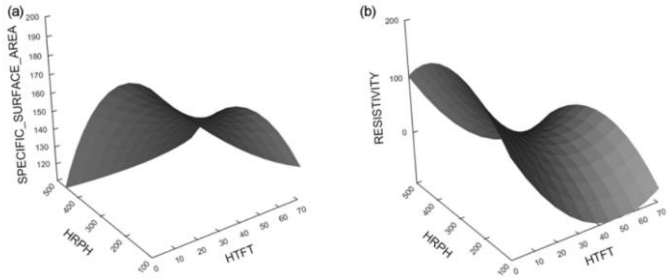

Figure 6. Effect of (a) HTFT and HRPH on specific surface area and (b) HTFT and HRPH on surface resistivity

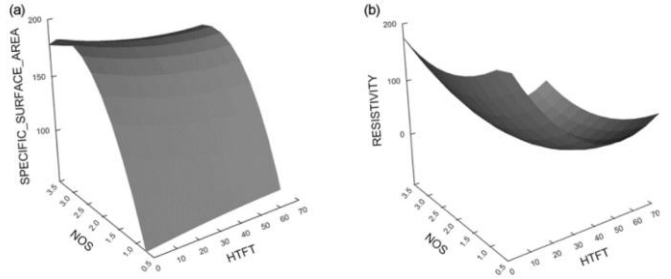

Figure 7. Effect of (a) HTFT and NOS on specific surface area and (b) HTFT and NOS on surface resistivity

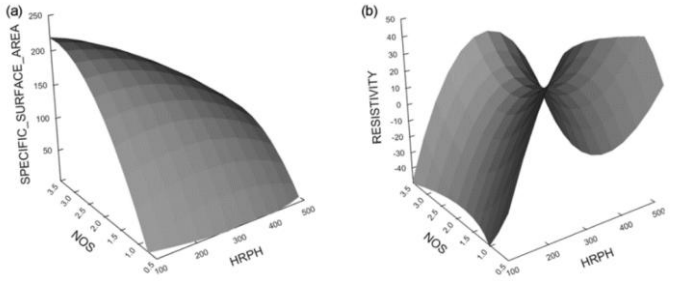

Figure 8. Effect of (a) HRPH and NOS on specific surface area and (b) HRPH and NOS on surface resistivity

4.4 Preparation of acrylic fibrous non-woven 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. After carding the web was transferred to needle punching machine to form a compact structure of non-woven web. The speed of feeding the carded web to needle punching machine was at the rate of 0.4 m/sec. The frequency of strokes was maintained at 200 (Strokes per minute) with the depth of needle penetration is 5 mm produced the web having thickness of 11.6 mm and density 2.78 g/cm^3. The schematic diagram for the formation of activated web is shown in figure 9. The acrylic fibrous web was then cut into 30 cm (length) and 20 cm (width) for subsequent high temperature treatment using high temperature furnace.

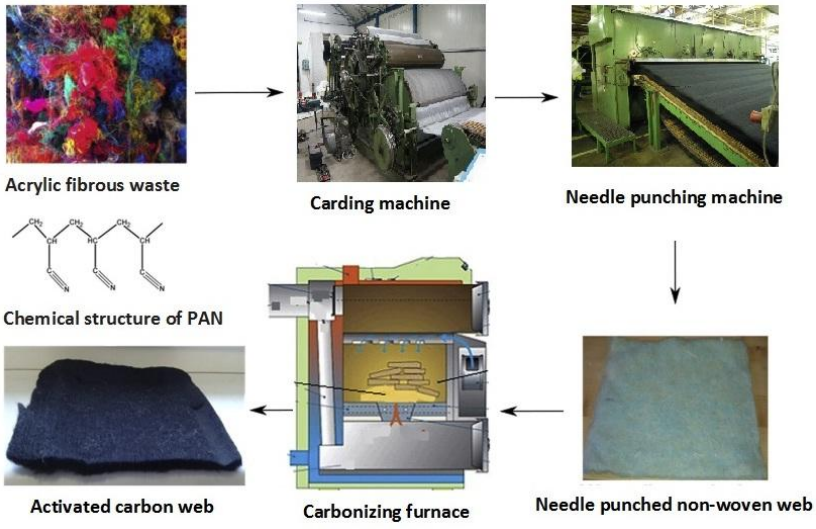

Figure 9. Schematic diagram of AC web from acrylic fibrous waste

4.4.1 Impact of tension during stabilization

The predetermined size of acrylic nonwoven web (30 cm×20 cm) was cut and transferred to high temperature furnace (Elektricke Pece Svoboda, Czech Republic). One web without tension and other webs with tension were stabilized in order to analyze changes in structure. The tension applied on the acrylic web during stabilization was found to affect the shrinkage and flexibility of prepared activated carbon webs. Figure 10 (a) and (b) shows the significant amount of shrinkage exhibited by stabilized web when there was no tension applied on acrylic web as compared when proper tension was applied on the web while stabilization. Shrinkage in

stabilized web is because of two reasons that is physical and chemical shrinkage. Stretching of acrylic fibers during their manufacturing develops strain in the molecules which relax during heat treatment hence shrinkage is observed in the fibers.

Figure 10. Activated carbon from stabilization (a) without any pre-tension, (b) with applied pre-tension

4.4.2 Characterization of activated carbon web prepared at different temperatures

Later the stabilized web was again heated to high temperature under the layer of charcoal for single stage carbonization and activation. The carbon webs were prepared at final temperature of 800 ˚C, 1000 ˚C and 1200 ˚C, with zero holding time and heating rate of 300 ˚C h^{-1}. After carbonization physical and analytical characterization was done on the prepared carbon webs. Physical characterization included yield %, shrinkage, flexibility and dusting properties. The yield of activated carbon before carbonization and after carbonization at different temperatures was calculated by using the equation 1.

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

When the temperature is increased from 800 ˚C to 1200 ˚C, the reaction of newly formed carbon with oxygen increased which resulted in decreasing yield of carbon and consequently shrinkage was increased and more rigid structure of activated carbon was achieved. Because of this reason activated carbon web at high temperature showed poor flexibility and dusting behavior as can be seen from table 7.

Table 7. Effect of carbonization temperature on physical properties of activated carbon web

Temperature [°C]	Yield [%]	Shrinkage	Flexibility	Dusting
800	61.27 ± 3.63	Good	Good	Good
1000	57.12 ± 1.83	Good	Average	Average
1200	45.11 ± 1.60	Average	Poor	Poor

Energy dispersive x-ray (EDS) analysis

It was performed on Oxford Instruments, LZ 5 EDX detector, UK to know the change in relative proportion of different elements with respect to change in carbonization temperature. From table 8, the increase in carbon content and reduction in oxygen content was found with increase in carbonization temperature from 800 °C to 1200 °C. The activated carbon web produced at 1200 °C exhibited 92.49% carbon content and 6.61% oxygen content. This behavior was attributed to removal of hydrogen, sulfur, nitrogen and other elements due to decomposition at higher temperature [25].

Table 8. Effect of carbonization temperature on elemental composition of activated carbon web

Element	App conc.	Intensity	Weight [%]	Atomic [%]
800 °C				
C K	0.26	2.12	0.13	91.76
O K	0.01	0.761	0.01	8.24
1000 °C				
C K	0.37	2.12	0.18	91.87
O K	0.02	0.760	0.02	8.13
1200 °C				
C K	0.18	2.10	0.09	92.49
O K	0.01	0.744	0.01	6.61
Ca K	0.00	0.902	0.00	0.90

X-Ray Diffraction (XRD) analysis

It was carried out on a PANalytical X0 Pert PRO MPD diffraction system. The development of crystalline and amorphous regions in prepared activated carbon web was investigated with respect to change in carbonization temperature. Degree of crystallinity can be calculated by using equation 2.

$$I_c = 1 - \frac{I_1}{I_2} \quad (2)$$

I_1 is intensity at minimum peak and I_2 is intensity at maximum peak [26].

Figure 11 shows the XRD pattern of different activated carbon samples produced at 800 ˚C, 1000 ˚C and 1200 ˚C temperature.

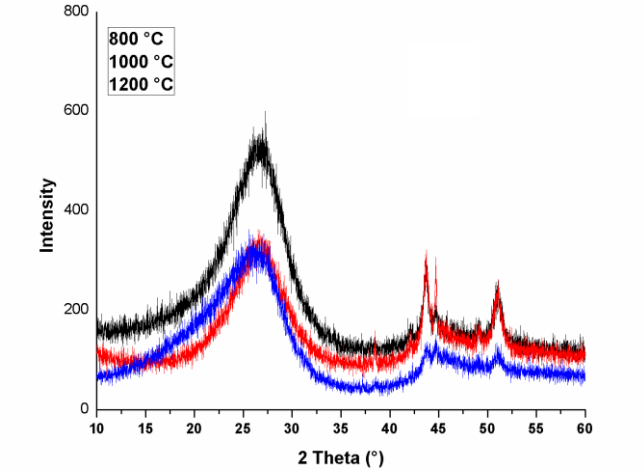

Figure 11. Effect of carbonization temperature on crystallinity of activated carbon web

The degree of crystallinity is increased from 82.21 % to 86.7 and then finally reached to 92.41% when the temperature was increased from 800 ˚C to 1000 ˚C and then finally to 1200 ˚C, which indicated higher crystallinity at high temperature due to more parallel orientation of chains.

SEM morphology

The field emission scanning electron microscope Sigma, Zeiss, Germany was employed to investigate the morphology of acrylic fibrous web and prepared activated carbon web of 800 ˚C, 1000 ˚C and 1200 ˚C carbonization temperature. This helped to understand the development of porosity characteristics of activated carbon web with change in carbonization temperature. Figure 12 (a-d) show the SEM images of acrylic fibrous web and activated carbon web produced at temperature of 800 ˚C, 1000 ˚C and 1200 ˚C respectively.

The activated carbon web showed noticeable rough surface as compared to acrylic fibrous web. The surface roughness was found to increase with increase in carbonization temperature, which indicated the development of more porous structure after physical activation of acrylic fibrous wastes. Further at high temperature carbonization due to more elimination of gases from acrylic fibers the diameters of fibers keep on decreasing as can be seen from figure 12 (a-d).

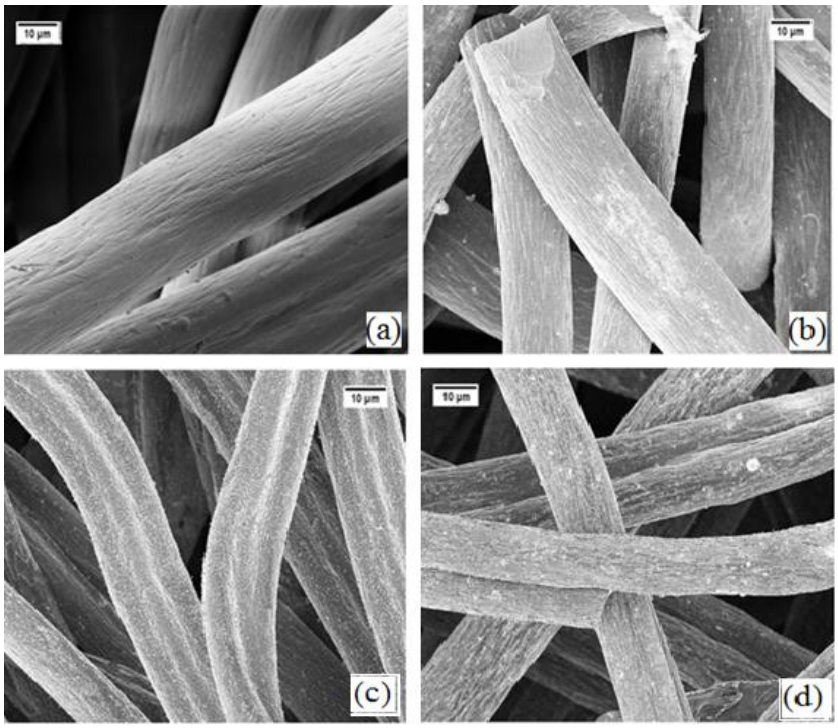

Figure 12. SEM image of (a) acrylic fibrous web (b) 800 ◦C activated carbon web (c) 1000 ◦C activated carbon web (d) 1200 ◦C activated carbon web

4.5 Results and discussions of electrical conductivity

The results of surface and volume conductivity of activated carbon webs are shown in table 9. The electrical resistivity was found to decrease with increase in carbonization temperature. The higher electrical conductivity of 1200 ˚C activated carbon sample was attributed to more graphitization, higher degree of crystallinity and carbon content which was confirmed from presence of sharp diffraction peak observed in XRD and EDX analysis.

Table 9. Surface and volume conductivity of AC webs

800 [˚C]	1000 [˚C]	1200 [˚C]
Parallel electrode (surface conductivity)		
0.3×10^{-2} [Ω^{-1}]	0.78 [Ω^{-1}]	3.7×10^{1} [Ω^{-1}]
Concentric electrode (surface conductivity)		
0.1×10^{-1} [Ω^{-1}]	0.354 [Ω^{-1}]	1.1×10^{1} [Ω^{-1}]
Concentric electrode (volume conductivity)		
3.34×10^{-5} [Ω-m]$^{-1}$	0.86×10^{1} [Ω-m]$^{-1}$	0.23×10^{2} [Ω-m]$^{-1}$

As the temperature during carbonization was increased, the degree of crystallinity also increased. The degree of crystallinity was found to be 82.21 %, 86.7% and 92.1 % at carbonization

temperature. 800 ˚C, 1000 ˚C and 1200˚C. Further at higher temperature the content of carbon also increased which is also another cause for increasing of electrical conductivity by increasing carbonization temperature as can be seen from table 9.

4.6 Results and discussions of EMI shielding effectiveness

4.6.1 EMI shielding effectiveness by wave guide method

Figure 13 (a-b) show the electromagnetic shielding effectiveness of prepared activated carbon webs in single and double layers measured at 2.45 GHz frequency. The electromagnetic shielding effectiveness was found to increase with increase in number of layers and increase in carbonization temperature. The electromagnetic shielding effectiveness of 28.29 dB, 26.06 dB and 3.34 dB was exhibited by single layers of activated carbon webs produced at 1200 ˚C, 1000 ˚C and 800 ˚C, respectively .The maximum shielding effectiveness in this range was attributed to increased multiple internal reflections and stronger absorption of electromagnetic radiations due to higher electrical conductivity, higher porosity and higher surface area [8]. The dramatic increase of shielding ability could not be expected with further increase of carbonization temperature (T > 1100 ˚C). Therefore, the usage of 1000 ˚C carbonization temperature was considered optimal with regard to its relatively high electromagnetic shielding ability and satisfactory mechanical properties. The similar trend was found for double layers of activated carbon, where shielding effectiveness was increased by 13% in case of 1000 ˚C activated carbon web. This behavior was attributed to increase in thickness with increase in number of layers [27].

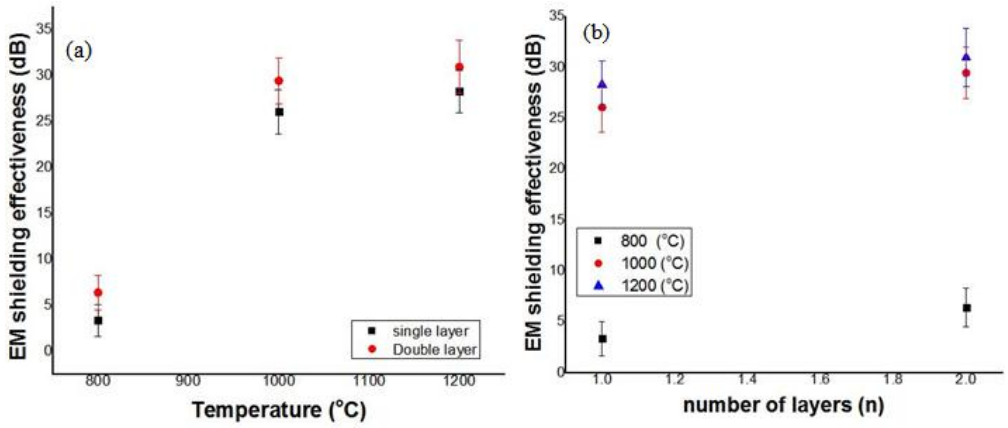

Figure13. (a). Effect of carbonization temperature on electromagnetic shielding effectiveness at 2.45 GHz (b). Effect of number layers on electromagnetic shielding effectiveness at 2.45 GHz

4.6.2 EMI shielding effectiveness by coaxial transmission line method

Figure 14 (a-b) show the shielding effectiveness for single layers of activated carbon samples in frequencies of 600 MHz, 1 GHz and 1.5 GHz. The increase in shielding effectiveness with increase in carbonization temperature was observed

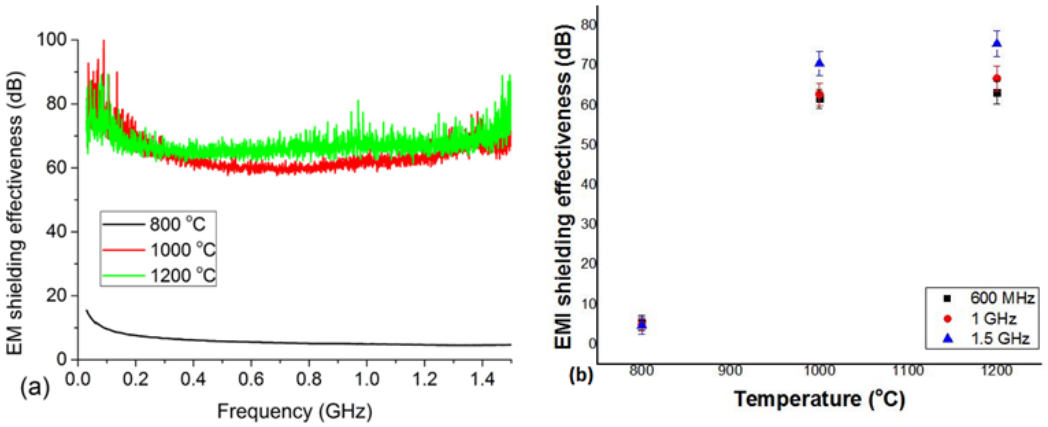

Figure 14.(a). Effect of frequency on electromagnetic shielding effectiveness (b) Effect of carbonization temperature on electromagnetic shielding effectiveness in low frequency region

The single layer of 800 ˚C activated carbon web revealed the lowest electromagnetic shielding effectiveness of about 5 dB in frequency range of 600 MHz-1.5 GHz. On the other hand, the 1200 ˚C activated carbon web exhibited the shielding ability of 63.26 dB, 66.75 dB and 75.44 dB for respective frequencies of 600 MHz, 1 GHz and 1.5 GHz.

4.7 Results and discussions for adsorption of methylene blue onto AC web

4.7.1 Effect of initial concentration of dye

In order to study the dye removal efficiency of prepared activated carbon web, it is important to investigate the effect of initial concentration of dye at first. Methylene blue solution of 50 mL was prepared in such a way that the initial concentration of dye varied from 2 to 10 mg L^{-1}. The quantity of 2 g L^{-1} activated carbon web was introduced as adsorbent in all different concentrations of dye solutions. Figure 15 (a) shows removal of dye percentage as a function of time and figure 15 (b) shows the derivative of dye removal with respect to time. It is clear that the percentage of dye removal increased with increase in contact time up to some extent and later reached a constant value when equilibrium is achieved. As the concentration of dye was increased, the time required to achieve the equilibrium was also increased. This can be explained by increased interaction of dye molecules with activated carbon [28].

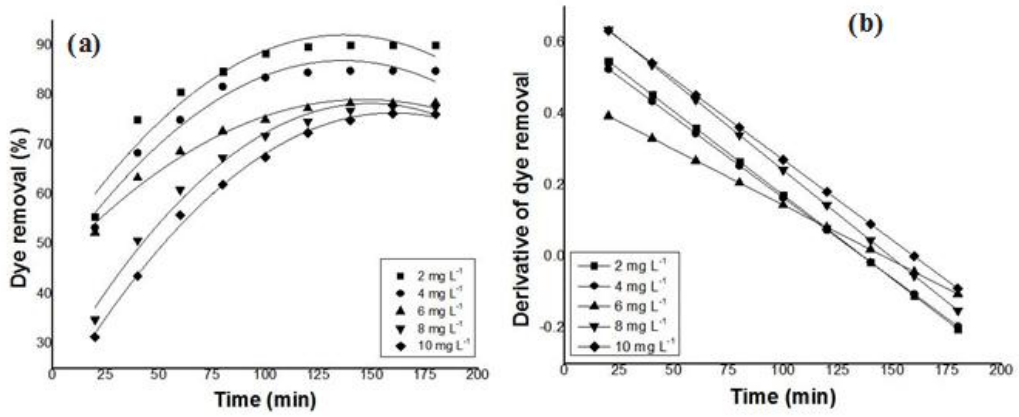

Figure 15 (a). Effect of initial dye concentration on adsorption performance (b).Derivative of initial concentration of dye on adsorption performance

At low concentration of dye, the increased interaction is because of less number of dye molecules as compared to high number of active sites on activated carbon surface. In other words, it took around 100 min to reach equilibrium when concentration of dye was less as compared to 140 min when the concentration of dye increased to 8.0–10.0 mg L^{-1}. As far as removal efficiency of dye was concerned, it decreased from 90.00 to 76.13% when initial concentration of dye increased from 2.0 to 10.0 mg L^{-1}. However, the total amount of methylene blue accumulated on activated carbon surface found to increase with the increasing initial concentration of dye. This behavior is related to presence of active sites on activated carbon surface for unit quantity of dye molecules available in the solution [28].

4.7.2 Morphology of activated carbon nonwoven web after dye adsorption

The SEM image of virgin and dye adsorbed activated carbon web is shown in figure 16 (a) & (b). It can be observed from figure 16 (a) that activated carbon web having rough surface with increased porosity after physical activation in high-temperature furnace. The dye removal behavior of prepared activated carbon can be justified from figure 16 (b) where adsorption of dye molecules was observed on the surface of activated carbon. The non-homogeneous adsorption of dye molecules is explained as a result of heterogeneous distribution of active groups and pores along the surface of activated carbon. The occurrence of big holes as observed in figure 16 (b) can be due to penetration of dye molecules through the pores of activated carbon surface or the elimination of trapped gases within the fiber during carbonization [29].

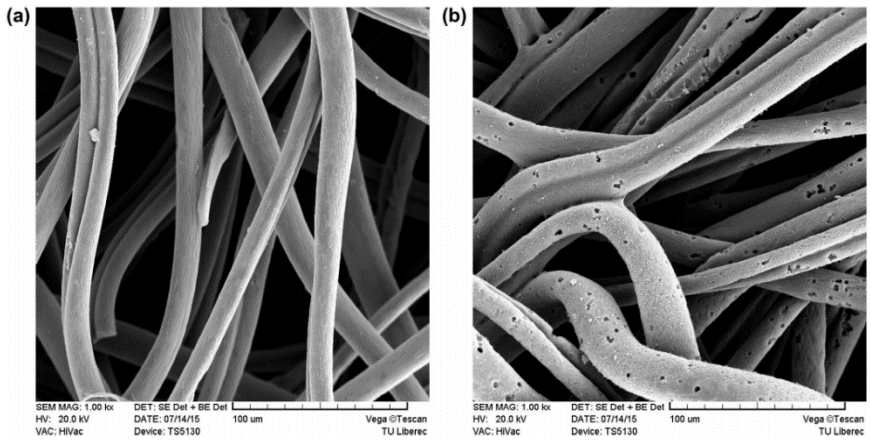

Figure 16. (a) SEM image of virgin activated carbon. (b) SEM image of dye adsorbed activated carbon.

4.7.3 Adsorption isotherms for adsorption of methylene blue onto AC web

Langmuir isotherms

The non-linear plot of q_e versus *Ce* for adsorption of methylene blue onto activated carbon at 30 °C is shown in figure 17 (a). The respective slope and intercept of plot q_e versus *Ce* were used to calculate the values of q_{max} and K_L as given in table 10. The values of their standard errors are also given in table 10. The coefficient of determination (R^2) determined from Langmuir isotherm was found 0.99 with the value of SSE 0.02. Moreover, the characteristics of Langmuir isotherm were described by dimensionless equilibrium parameter (R_L) as given in equation 3. The R_L value of 0.36 showed favorable adsorption of methylene blue onto activated carbon.

$$R_L = \frac{1}{1+K_L C_o} \tag{3}$$

Table 10. Parameters for adsorption isotherms

Langmuir adsorption isotherm		Freundlich adsorption isotherm	
q_{max} [mg g^{-1}]	8.76 ± 1.16	K_F	1.93 ± 0.01
K_L [L mg^{-1}]	0.29 ± 0.05	1/n	0.71 ± 0.02
R_L	0.36	R^2	0.99
R^2	0.99	SSE	0.00
SSE	0.02	K_F	1.93 ± 0.01

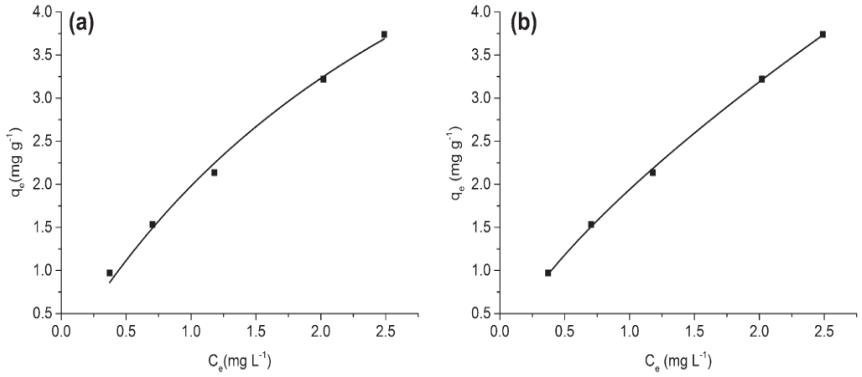

Figure 17. (a) Langmuir adsorption isotherm. (b) Freundlich adsorption isotherm

Freundlich isotherms

The Freundlich plot for adsorption of methylene blue onto activated carbon at 30 ˚C is shown in figure 17 (b). The respective intercept and slope of plot C_e versus q_e were used to calculate the values of K_F and *1/n as* given in table 10. The value of SSE in Freundlich adsorption isotherm was found lower than Langmuir adsorption isotherm, which explained closer fit of results with Freundlich model. This indicated more heterogeneous surface nature of prepared activated carbon having nonhomogeneous distribution of active groups on their surface. Nevertheless, the value of *1/n* is close to 1 (i.e. 0.71) in Freundlich model which revealed the physical adsorption of methylene blue on homogeneous surface nature of activated carbon [30]. This further suggested that both Langmuir and Freundlich models could be applicable for present study.

4.8 Preparation of iron impregnated activated carbon web

From the acrylic web a piece of 30 cm × 20 cm was cut. The sample was washed with distilled water to remove any impurity and then placed in oven at 100 ˚C for 4 to 5 hours to make it complete dry. Then the dried sample was immersed in solution of ferric chloride and boiled for four hours, then it was washed with distilled water in order to remove extra iron content. The sample was then again placed in oven at 100 ˚C for 4 to 5 hours to make it completely dry. The iron impregnated acrylic web was then transferred to high temperature furnace for further heat treatment. Initially the web was stabilized at 250 ˚C with a heating rate of 50 ˚C hr^{-1}. The sample was stabilized so that they it can stand against further high temperature treatment. The stabilized sample was again heated at 1200 ˚C with a heating rate of 300 ˚C hr^{-1} under the layer of charcoal for physical activation.

The specific surface area was measured from N_2 adsorption-desorption isotherms at 77.35 K using Quantachrome Instruments. Adsorption/desorption isotherm measurements were collected in the relative pressure range P/P_o from 0.02 to 1. Both adsorption and desorption isotherms were measured and the specific surface area was determined. The specific area of AC and FeAC was found to be 280 m^2g^{-1} and 570 m^2g^{-1}.

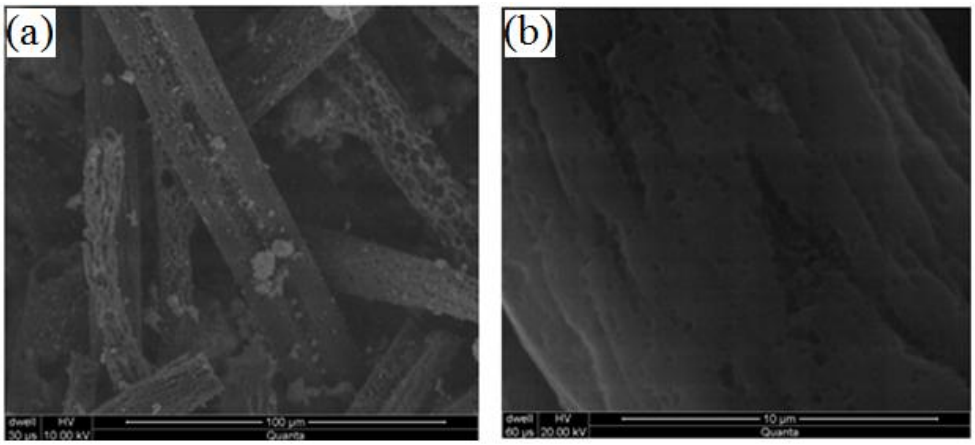

Figure 18. (a) SEM image of AC and (b) SEM image of FeAC

The specific surface area of AC and FeAC was found to be 280 m^2g^{-1} and 570 m^2g^{-1} by using BET surface area. For the better understanding of surface characteristics, SEM analysis of activated carbon prepared from acrylic waste and iron impregnated activated carbon was analyzed. The SEM image of both the activated carbon with iron content and without iron content can be seen from figure 18 (a) and (b).

4.9 Results and discussions for adsorption of methylene blue onto iron impregnated AC web

4.9.1 Effect of initial dye concentration

The adsorption performance of iron impregnated activated carbon was studied by varying the dye concentration from 10 mg L^{-1} to 50 mg L^{-1}. It was found that removal percentage of methylene blue and adsorption capacity of adsorbent increases with increase of time as shown in figure 19 (a) and (b). The reason for smaller equilibrium time at low concentration of dye is because of relatively more number of active sites available for adsorption of dye molecules. It took around 90 minutes to reach to the equilibrium when concentration of dye was at 10 mg L^{-1} as compared to around 120 to 135 minutes when the dye concentration was increased from 40

mg L^{-1} to 50 mg L^{-1}. As far as the removal of dye is concerned, it decreased from 97.05 % to 84.41 % keeping other parameters constant like temperature, stirring speed and adsorbent dosage. As far as dye accumulation on adsorbent is concerned, it increased with increase in concentration of dye. The dye accumulated on iron impregnated activated carbon is found to increase from 3.74 mg g^{-1} to 19.56 mg L^{-1} when the dye concentration was increased from 10 mg L^{-1} to 50 mg L^{-1}. This behavior is obvious due to the availability of active sites in adsorbent for the unit quantity of methylene blue in the solution [31].

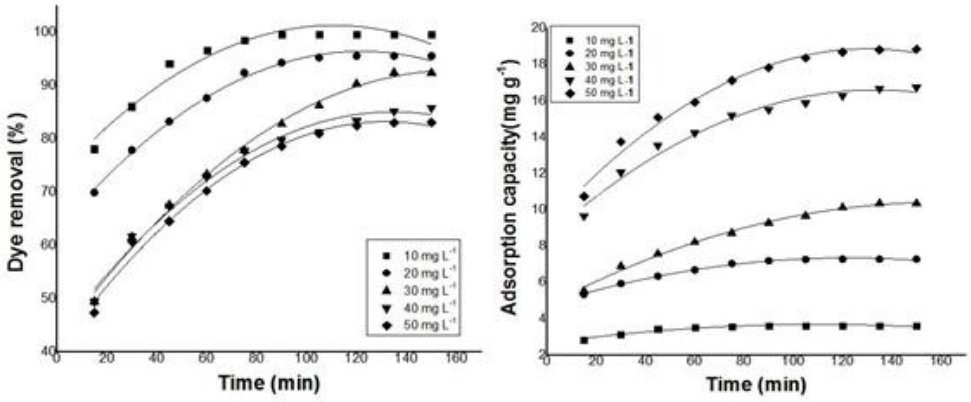

Figure 19. (a) Effect of initial dye concentration on dye removal at constant and (b) effect of initial dye concentration on adsorption capacity at constant (shaking speed: 200 rpm, pH=7, dosage=0.1 g)

4.9.2 Adsorption isotherms for adsorption of methylene blue onto iron impregnated AC web

Langmuir isotherm

The linear form of Langmuir isotherm was plotted by taking q_e/ce on y-axis and q_e on x-axis. From the slope and intercept of figure 20 (a), the value of q_{max} and K_L were calculated. The value of correlation coefficient from linear plot of Langmuir was found 85.20, which indicated the mono layer adsorption. Since, the value of correlation coefficient was not very good so the non-linear form of Langmuir was also plotted by taking q_e on y-axis and C_e on x-axis as shown in figure 20 (b). The parameters of both the linear and non-linear forms of Langmuir mode are mentioned in table 11.

Freundlich Isotherm

The linear form of Freundlich model was drawn by taking *ln* C_e on x-axis and *ln* q_e on y-axis as shown in figure 20 (c). From the slope and intercept of this line, the values of *1/n* and k_F were calculated. The non-linear form of Freundlich model was drawn by taking C_e on x-axis and q_e on y-axis as shown in figure 20 (d). The values of non-linear and linear form of Freundlich model are also mentioned in table 11. The higher values of correlation coefficient indicated that Freundlich model fit closely as compared with Langmuir model.

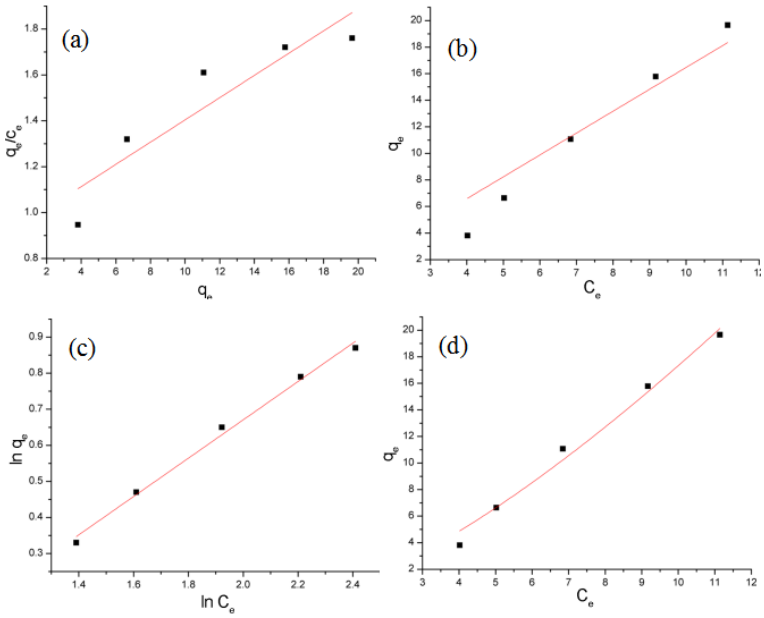

Figure 20. Linear and non-linear forms of Langmuir and Freundlich isotherms

Table 11. Parameters of Langmuir and Freundlich isotherms for sorption of methylene blue on FeAC

	Langmuir isotherm			Freundlich isotherm		
	R^2	K_L [L mg^{-1}]	q_{max} [mg g^{-1}]	R^2	K_F [mg g^{-1}]	n
Linear regression	85.20	0.052	20.61	99.21	0.39	1.88
Non-linear regression	89.98	4.01	4.10	98.18	0.70	0.72

4.9.3 Adsorption kinetics for adsorption of methylene blue onto iron impregnated AC web

The kinetics of adsorption for methylene blue onto FeAC were studied by fitting the experimental data to linear and non-linear forms of pseudo first and pseudo second order models respectively. The linear and non-linear plots of pseudo first and pseudo second order models

have been presented in the figure 21. Both the linear forms of pseudo first and pseudo second order models showed trend of mutual relationship and their values are given in table 12 and 13. The values of k_1, q_e, k_2 and q_2 are calculated from slope and intercept of figure 21 (a & c).

Table 12. Parameters of pseudo first order (linear and non-linear model)

Kinetic models parameters	Initial concentrations [mg L^{-1}]				
	10	20	30	40	50
$q_{e,exp}$ [mg g^{-1}]	3.77	6.64	11.07	15.84	19.65
Pseudo first order linear model					
$q_{e,exp}$ [mg g^{-1}]	0.312	0.58	0.88	1.08	1.349
K_1 [min^{-1}]	-0.02	-0.017	-0.011	-0.012	-0.016
R^2	0.98	0.95	0.99	0.95	92.07
Pseudo first order non-linear model					
$q_{e,exp}$ [mg g^{-1}]	3.69	6.42	10.55	15.07	18.88
K_1 [min^{-1}]	0.09	0.083	0.047	0.049	0.044
R^2	80.4	78.74	89.68	87.32	86.76

Table 13. Parameters of pseudo second order (linear and non-linear model)

Kinetic models parameters	Initial concentrations [mg L^{-1}]				
	10	20	30	40	50
$q_{e,exp}$ [mg g^{-1}]	3.77	6.64	11.07	15.84	19.65
Pseudo second order linear model					
$q_{e,cal}$ [mg g^{-1}]	0.253	0.14	0.08	0.05	0.044
K_1 [min^{-1}]	1.41	1.11	1.38	0.94	0.84
R^2	99.29	99.56	99.90	98.80	99.78
Pseudo second order non-linear model					
$q_{e,cal}$ [mg g^{-1}]	3.95	6.96	12.15	17.29	18
K_1 [min^{-1}]	0.04	0.02	0.005	0.003	0.002
R^2	97.56	97.29	98.38	97.96	97.14

Table 12 & 13 gives the values of rate constant and methylene blue uptake at different concentrations of dye. In linear forms the correlation coefficient values of pseudo second order model are more appropriate than the pseudo first order, however the values of dye uptake are far from practical values. The non-linear curve fitting was done with the help of origin pro as can be seen from figure 21 (b & d). In non-linear forms both the models gave values that are more close to the practical results. However the values of R^2 for pseudo second order are more appropriate than pseudo first order. Hence by comparing the results of both linear and non-linear forms of

pseudo first and pseudo second order model, it is concluded that adsorption behavior of methylene blue onto FeAC followed non-linear form of pseudo second order [32].

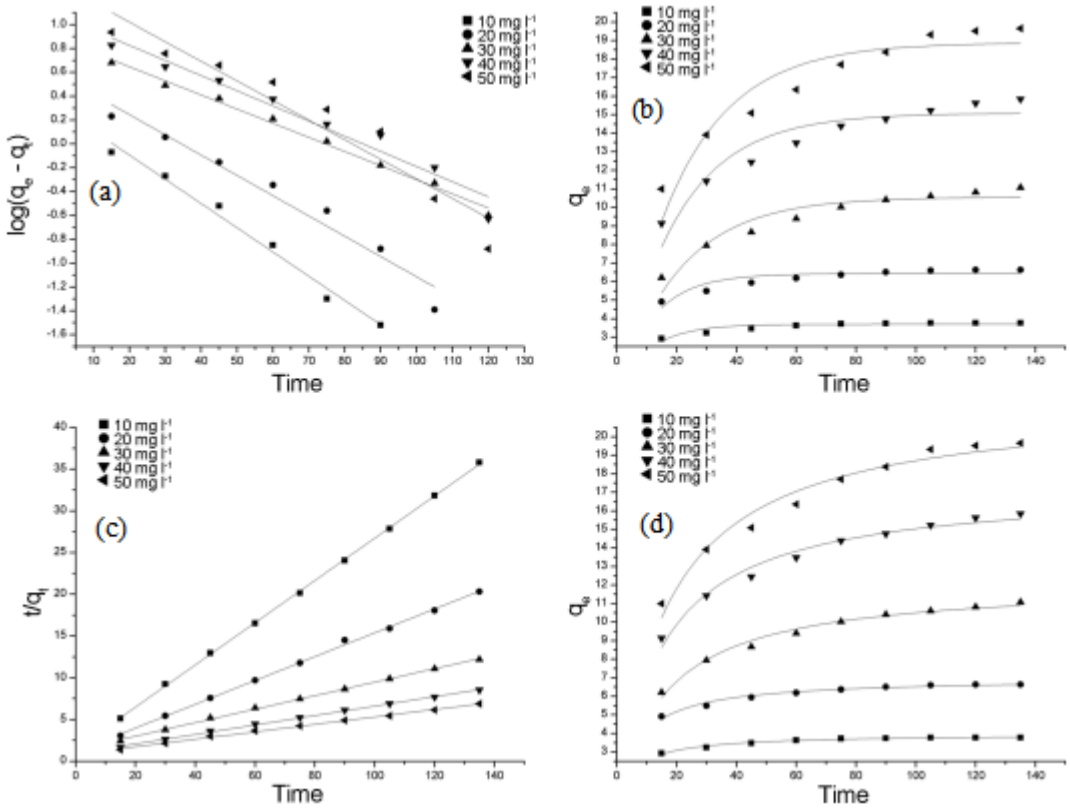

Figure 21. Linear and non-linear forms of pseudo first order and pseudo second order model

5 Conclusion and future work

The following conclusions were drawn on each study.

5.1 Optimization of carbonization parameters

The acrylic fibrous waste was successfully converted into activated carbon by physical activation in the presence of air using controlled thermal treatment in high temperature furnace. The multistage pyrolysis with 1200 ˚C of final pyrolysis temperature resulted into activated carbon having higher specific surface area and higher electrical conductivity. The lower heating rate and shorter holding time were found to have significant effect on the development of porous morphology with higher surface area. This behavior is attributed to gradual reaction of atmospheric oxygen with carbonized acrylic fibrous waste. From the achieved results it was

found that among three heating rate (150, 300 and 450 $^{\circ}C\ hr^{-1}$), 300 $^{\circ}C\ hr^{-1}$ was best choice for getting higher surface area and electrical conductivity along with two number of steps at 1200 $^{\circ}C$. Although by using single step electrical conductivity was good but yield of activated carbon fibers was very less. On the basis of finalized parameters the acrylic fibrous web was carbonized to get porous and electrically conductive web.

5.2 Physical properties of activated carbon web

In terms of physical properties of activated carbon webs the yield %, shrinkage, flexibility and dusting properties were analyzed.

- It was found that by increasing temperature from 800 $^{\circ}C$ to 1000 $^{\circ}C$ and 1200 $^{\circ}C$, the yield of carbon web was decreased from 61.27 % to 57.12 % and finally 45.11 %.
- However substantial shrinkage in activated carbon web was also observed. By increasing temperature, more reactions of carbonizing material causes elimination of volatile gases and tarry matter resulted in higher content of carbon although a decrease in the yield of carbon. The decrease or reduction in yield and shrinkage can also be seen from SEM images that at higher temperature size of fibers decreased.
- Likewise at high temperature more carbonization causes reduction in flexibility of webs which also caused adverse effects on the dusting properties of activated carbon webs.

5.3 Electrical properties of activated carbon webs

The surface electrical conductivity of activated carbon webs prepared at 800 $^{\circ}C$, 1000 $^{\circ}C$ and 1200 $^{\circ}C$ was measured by using parallel electrode and concentric electrode methods. However concentric electrode method was used for volume conductivity of webs as well.

- Both the methods showed that by increasing carbonization temperature conductivity kept on increasing due to more graphitization, crystalline content and higher percentage of carbon content.
- By increasing temperature from 800 $^{\circ}C$ to 1200 $^{\circ}C$, the carbon content was increased from 91.76 % to 91.87 % and finally to 92.49 %. However the crystalline content increased from 82.21 % to 86.71 and to 92.41% when the carbonization temperature was increased from 800 $^{\circ}C$ to 1000 $^{\circ}C$ and 1200 $^{\circ}C$ respectively.

5.4 EMI shielding effectiveness of activated carbon webs

This study was focused on the development of porous and electrically conductive activated carbon based electromagnetic shielding materials from acrylic fibrous wastes. This was achieved by physical activation of needle punched nonwoven web of acrylic fibers. The utility of prepared activated carbon webs were investigated for electromagnetic shielding ability in high frequency (i.e. 2.45 GHz) and low frequency regions (i.e. below 1.5 GHz) using waveguide method and coaxial transmission line method, respectively. At 2.45 GHz, the electromagnetic shielding effectiveness of 28.29 dB, 26.06 dB and 3.34 dB was exhibited by single layers of activated carbon web produced at 1200 °C, 1000 °C and 800 °C, respectively. On the other hand, for low frequency regions, the 1200 °C activated carbon web exhibited the shielding ability of 63.26 dB, 66.75 dB and 75.44 dB for respective frequencies of 600 MHz, 1 GHz and 1.5 GHz. This behavior was attributed to increased multiple internal reflections and stronger absorption of electromagnetic radiations, which resulted from greater number of nomadic charges (i.e. graphite content), uniform dispersion of graphite layers, reduced fiber diameter, elongated electrons' mean free paths, larger surface area, higher porosity and enhanced conductive network formation in 1200 °C activated carbon.

5.5 Removal of methylene blue from activated carbon

The multistage pyrolysis with 1200 °C temperature, 300 °C $h^{-1}$of heating rate without any holding time revealed the higher specific surface area (280 m^2 g^{-1}). In subsequent step, the adsorption performance of methylene blue onto prepared activated carbon web was investigated. Methylene blue removal efficiency was checked at different process parameters by varying initial dye concentration, adsorbent dosage, different stirring speed, and pH value of solution. The results indicated that the adsorption of methylene blue on activated carbon required higher equilibrium time. However, when adsorbent dosage and stirring speed was increased, the removal of dye required less time. When the obtained results were compared with adsorption isotherms (i.e. Langmuir and Freundlich isotherms), the Freundlich model was found to fit closely with results due to heterogeneous adsorption of dye molecules on activated carbon surface.

5.6 Removal of methylene blue after iron impregnation

The acrylic fibrous waste was successfully converted into activated carbon and iron impregnated activated carbon through physical activation by using thermal treatment process in the high temperature muffle furnace. The higher surface area was obtained with iron impregnated activated carbon (570 m^2 g^{-1}) as compared with AC (280 m^2 g^{-1}). The high temperature carbonization process was carried out at 1200 $^{\circ}C$ hr^{-1} with no holding time after carbonization. Controlled atmospheric oxygen reacted with carbon under slow heating rate for getting higher surface area. In case of iron impregnated activated carbon web, the breaking of carbon-carbon bonds happened and iron deposited on AC through physical and chemical attachment. This phenomenon was mainly responsible for the reduction of crystallinity and more porous structure in FeAC as compared to AC. The surface charge density of activated carbon decreased from 6.7 to 4.8, because of iron impregnation and surface oxidation. This acidic nature of FeAC was found to be important for the uptake of cationic dyes like methylene blue from waste water. The adsorption phenomenon in terms of adsorption capacity and dye removal percentage was investigated by varying dye concentration, adsorbent dosage, different stirring speed and pH (2-10) values of solution. The results showed that dye removal time was increased, when the concentration of dye increased in the solution. However, dye removal time can be reduced by increasing stirring speed and adsorbent dosage at suitable pH value. The results were analyzed by using adsorption isotherms (linear and non-linear forms of Langmuir and Freundlich) and adsorption kinetics (linear and non-linear forms of pseudo 1st and pseudo 2nd order models). By comparing the results of pseudo first and second models, it was found that non-linear models give more reliable and close results with experimental values. It was also observed that Freundlich model fit more closely to the data. This is because the surface of FeAC is not homogenous due to different deposition of iron and porosity. The SEM results also showed the heterogeneous distribution of iron particles on FeAC. On the basis of this study, it was concluded that iron impregnation before carbonization can be effectively employed for the removal of cationic dyes from waste water.

5.7 Proposed applications and limitations

The proposed applications of activated carbon web is eco-friendly usage for EMI shielding. The same web can be used as interlining for the EMI shielding purpose in protective clothing. It has also good application for ohmic heating especially for heating indoor applications. Due to porous morphology this web can be used for the removal of bad and poisonous gases and also finds strong application in textile waste water effluents especially after impregnating it with some salt like iron chloride. In spite of positive aspects the main drawback of this method is a less yield as compared with the preparation of carbon in inert atmosphere but by using this method cost factor can be significantly reduced. But the idea of using acrylic fibrous waste for the formation of activated carbon web is a good prospect towards using waste material for reducing the cost of activated carbon.

5.8 Future work

- Chemical activation for the creation of more porous structure.
- Preparation of high loft non-woven for comparison of electrical properties with needle punched web.
- Effect of different temperatures and voltages on the electrical conductivity (surface and volume) for needle punched high loft non-woven webs.
- Impact of thickness on the carbonization behavior for determining EMI shielding effectiveness.
- Investigation of carbon web characteristics prepared by using inert atmosphere with the settings proposed by this method.
- Comparison of structural characteristics of activated carbon prepared from physical and chemical activation
- Study on carbonization of nano-fibrous acrylic membranes.

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7 List of publications by the author

7.1 List of publications in research journals

1. Baheti V, Naeem S, Militky J, Okrasa M, Tomkova B. Optimized preparation of activated carbon nanoparticles from acrylic fibrous wastes. Fibers and Polymers. 2015; 16:2193-201. **(Impact factor = 1.20).**
2. Salman Naeem, Vijay Baheti, Jiri Militky, Jakub Wiener, and Jaromir Marek: Removal of methylene blue from aqueous media using activated carbon web, Journal of Textile Institute. vol. 108 (2017) , no. 5, pp. 803–811 **(Impact factor = 1.128).**
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4. Salman Naeem, Vijay Baheti, Veronika Safarova, Jiri Militky, Blanka Tomkova. Development of porous and electrically conductive activated carbon web for effective EMI shielding applications. Carbon, vol. 111 (2017), pp. 439-447. **(Impact factor = 6.198).**
5. Naeem S, Baheti V, Militky J, Wiener J. Sorption properties of iron impregnated activated carbon prepared from acrylic fibrous waste. **vlákna a textile**, September 2016.

7.2 List of book chapters

1- Baheti V, **Naeem S**, Militky J, Mishra R, Tomkova B, Kremenakova D. Activated carbon nano particles from acrylic fiber waste. Progress in Fibrous Material Science 1. ed, ISBN 978-80-87269-40-4.
2- Baheti V, Faheem S, **Naeem S**, Prusova M, Militky J. Novel strategies for flame retardant high loft polyester non wovens. *Recent developments in fibrous material science*. 2015; 364-383. ISBN 978-80-87269-45-9.
3- **Naeem S**, Baheti V, Militky J, Javed S, Wiener J, Marek J. Activated carbon sorbents from acrylic fibrous wastes. *Recent developments in fibrous material science*. 2015; 384-402. ISBN 978-80-87269-45-9.
4- **Naeem S,** Baheti V, Militky J, Wiener J, Javed S, Ashraf A, Marek J, Khan N. Removal of methylene blue from aqueous solutions by using iron impregnated activated carbon web from waste acrylic fibres. Advances in fibrous material science. 2016; 347-363. ISBAN 978-80-87269-48-0.

7.3 List of publications in international conferences

1- **Salman Naeem**, Vijay Baheti, Jiri Militky, Malgorzata Okrasa, Blanka Tomkova.Utilization of acrylic fibrous waste for preparation of activated carbon nanoparticles, 90thTextile Institute World Conference 2016, Poznan, Poland.

2- Vijay Baheti, **Salman Naeem**, Jiri Militky, Rajesh Mishra, Blanka Tomkova. Optimum pyrolysis of waste acrylic fibers for preparation of activated carbon. Textile Bioengineering and Informatics Symposium 2015, Zadar, Croatia, pp. 7 – 14. ISSN. 1942-3438.

3- Vijay Baheti, **Salman Naeem**, Rajesh Mishra, Jiri Militky, Blanka Tomkova: Optimized pyrolysis conditions of carbon black particles preparation from waste acrylic fibers, AUTEX, June 2015, Bucharest, Romania.

4- **Salman Naeem,** Vijay Baheti, Jiri Militky, Jakub Wiener. Removal of methylene blue from aqueous solution by using iron impregnated activated carbon web from waste acrylic fibers. XXIV. IFATCC conference Pardubice, 2016.

5- **Salman Naeem**, Qummer Zia Gilani, Vijay Baheti, M. Azeem Ashraf, Jiri Militky, Jakub Wiener, Jaromir Marek. Application of activated carbon web for efficient removal of methylene blue. 22nd-25th September. Workshop Světlanka 2015.

6- **Salman Naeem**, Saima Javed, Vijay Baheti, Jiri Militky, Zuhaib Ahmed, Promoda Behera. Effect of temperature, heating rate and holding time on the properties of carbon web from acrylic waste.

8 Curriculum Vitae

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Book Chapters

- Baheti V, **Naeem S**, Militky J, Mishra R, Tomkova B, Kremenakova D. Activated carbon nano particles from acrylic fiber waste. Progress in Fibrous Material Science 1. ed, ISBN 978-80-87269-40-4.
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- **Naeem S**, Baheti V, Militky J, Javed S, Wiener J, Marek J. Activated carbon sorbents from acrylic fibrous wastes. *Recent developments in fibrous material science*. 2015; 384-402. ISBN 978-80-87269-45-9.

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Record of the state doctoral exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

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Studijní obor: **Textile Technics and Material Engineering**

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V Liberci dne 30. 11. 2016

O průběhu SDZ je veden protokol.

Recommendation of the supervisor

Supervisor's opinion on PhD thesis of Muhammad Salman Naeem

Topic: Development and Application of Activated Carbon Web Prepared from Acrylic Fibrous Waste

I am writing this recommendation letter for Muhammad Salman Naeem regarding his final defense. Mr. Muhammad Salman Naeem has been studying and doing research work under my supervision for the last three and half years. He is intelligent, positive minded, agile and good in research work.

The main objective of this research work was to use acrylic fibrous waste for the formation of activated carbon and to find suitable applications. The optimization of parameters for getting higher values of surface area and electrical conductivity have been successfully performed. XRD, SEM, EDX and BET analysis were performed to analyze change in structure and surface at different temperatures. Later the developed activated carbon web was successfully employed for electrical conductivity, EMI shielding application and adsorption performance was evaluated with and without metal impregnation.

The thesis is well written, concise and compact. His publications are quite worthy and good addition in the field of activated carbon. He has published 4 (Four) papers in impact factor journals (another 2 papers are under review), 1 (One) in Scopus indexed journal, 3 (Three) book chapters and 6 (six) presentations in international conferences.

By concluding I can say that it is a novel method for converting acrylic fibrous waste into activated carbon. I strongly recommend him for the defense as he has completed all the necessary requirements and good work he has done.

27.03.017

prof. Ing. Jiří Militký, CSc. EURING

Supervisor

Opponent's reviews

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-17/4814/025822, dated 26. 6. 2017) of **Muhamad Salman Naeem, M.Sc.** entitled **"Development of Activated Carbon Web from Acrylic Fibrous Waste"**. Tutor of the PhD. student was Prof. Ing. Jiří Militký, CSc.

Theses presented has a technological impact for using of acrylic fibrous waste together with a novel methods of single stage carbonization and activation by using physical activation under the layer of charcoal.

The main objective is to convert acrylic fibrous waste into activated carbon fibrous for getting higher surface area and electrical conductivity by optimization of parameters for temperature, heating rate, holding time and so on.

Major results of the thesis are focused on optimization of carbonization parameters, physical and electrical properties of activated carbon web and EMI shielding effectiveness. Next part of thesis is removal of methylene blue from activated carbon and after iron impregnation of surface.

Iron impregnated activated carbon and non-impregnated characterization as the adsorption substrate was studied by means of adsorption isotherm determination BET (pore size and specific surface area determination), Freundlich and Langmuir isotherms and adsorption kinetics determination for a given pair of adsorption material and adsorbing substrate methylene blue. Adsorption capacity of the tested materials was performed at various dyes concentration, stirring speed and pH. The chosen methods fully characterize adsorption profile of the tested material for given application. Furthermore, there were applied methods of X-ray analysis, SEM morphology, electrical conductivity, waveguide method and coaxial transmission line method for electromagnetic shielding ability.

Applied methods used by the applicant were modern current measuring techniques and give exhaustive information about the studied material and its use.

Proposed application of activated carbon web for ohmic heating especially for heating indoor applications seems promising from the practical point of view.

From the formal point of view, results of the theses and the thesis itself are well written, results are presented in the form of tables and graphs. Thesis represent typical material science oriented study focused on polymeric fibers characterization for textile industry.

Thesis are written in English language in the form of the monograph. Thesis total references cited was 114. There were cited fundamental research articles as well as the latest publications. However the format of the reference list is not fulfilling requirements of the citation standard CSN ISO 690.

Results of the thesis of the applicant Naeem S. were published in 4 scientific papers in impacted journals and one more paper in XXIV International Congress IFATCC 2016. He was attending several scientific conferences at home as well as abroad, he is the author and coauthor of 3 contribution in the book Chapters.

Questions to be answered during thesis defense:

1) Have you tested AC web for adsorption without impregnation as well?

2) Have you performed desorption experiments too?

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Muhamad Salman Naeem, M.Sc. for defense.

In Zlin, July 28, 2017

Doc. Mgr. Barbora Lapčíková, Ph.D.

Associated professor for materials science and engineering
Tomas Bata University in Zlin

Referee´s report on PhD. thesis of

Muhammad Salman Naeem

„ Development of Activated Carbon Web from Acrylic Fibrous Waste“

Professor Miroslav Černík

The presented thesis consists of 105 pages and appendix including 5 scientific publications. The thesis is divided into 7 major chapters plus References and List of publications. The thesis deals with production and characterization of carbon fibres from textile materials.

Abstract summarizes content of the thesis and major results.

Chapter 1 (Introduction) is about background of the topic – production of carbon fibres. The process starts from acrylic fibrous waste through mechanic cutting, impregnation with iron salt and stabilization at 250°C till final carbonization at 800 till 1200°C.

Chapter 2 (Research objectives) defines objectives of the thesis – optimize parameters for preparation of activated carbon fibres, prepare porous and electrically conductive activated carbon web, application of the carbon fibres for electromagnetic shielding, and determination of sorption properties of activated carbon.

Chapter 3 (Literature review) starts with description of carbon allotropes including graphite, diamond, amorphous carbon, fullerene and carbon nanotubes. I would expect here more deep description of the allotropes, their properties and especially for graphene,which is not consider as the most progressive carbon material. Also included Figure 3 is without capture. Next subchapter is about activated carbon, which is the topic of the thesis. The author specifies different types, source materials, where PAN is described with sufficient details including conversion to activated carbon. Important properties specified are connected with thesis objectives specified above.

Chapter 4 (Research Methodology) deals with methods used for preparation of carbon fibres and their characterization. Basic methods used are EDX, XRD, SEM, BET, EMI shielding, coaxial transmission line method, adsorption study with methylene blue.

Chapter 5 (Results and discussion). Great advantage of this chapter is that results presented here were already published in scientific papers, included in the annexes of the thesis. The papers were peer reviewed and therefore the scientific and technical quality of the result was already positively evaluated. The chapter starts with optimization of pyrolysis parameters. Important part is characterization of AC webs prepared at different temperatures (EDX, XRD, SEM, BET, electric conductivity). Important properties are the electromagnetic shielding effectiveness of prepared activated carbon and adsorption. Interesting results are linear dependencies of derivative dye removal on time, adsorbent dosage, stirring time and pH.

Chapter 6 (Conclusion and future works) summarizes the determined results of the thesis.

Results showed that all studied parameters have significant influence to quality and production amount of carbon fibres. Highest temperature 1200°C of the final hydrolysis resulted in higher specific surface area (280 m^2/g) and electric conductivity. Question is, why other temperatures were not studied, e.g. 1300°C? Is there any limit of resulting fiber stability? Of course yield of carbon web decreases with increasing temperature. Flexibility also decreases with the temperature.

Author determined that by increase of temperature from 800 to 1200°C, the carbon content was increased from 91.76% to 91.87% and finally to 92.49%. What is the result variability? Are these changes significant or it is just in range of experimental error? This is also reason for increase of electric conductivity (together with increase in crystallinity).

Study of methylene blue adsorption showed the Frendlich adsorption model fitted the data more precisely compare to Langmuir model. Author relates this with heterogeneous adsorption of dye molecule on activated carbon surface. Which heterogeneity is meant? Heterogeneity of C-sites on the surface? Heterogeneity of dye?

Referee remarks, question and conclusions

The thesis is logically divided into chapters, the content is explained illustratively, and all determined results are simply described.

QUESTIONS

1. Why other temperatures for final carbonization were not studied, e.g. 1300°C?
2. Author determined that by increase of temperature from 800 to 1200°C, the carbon content was increased from 91.76% to 91.87% and finally to 92.49%. What is the result variability? Are these changes significant or it is just in range of experimental error?
3. Which heterogeneity of adsoption the author meant? Heterogeneity of C-sites on the surface? Heterogeneity of dye?

Imperfections and recommendations

Language of the thesis is very good and thesis is nicely written. I did not find many errors and mistypes.

Referee´s conclusion

The presented thesis is logic, has all necessary parts and show the author understand his work and he is able to put results logically into appropriate parts. There are no significant recommendations for next author´s work. The language is good and fully understandable. The main advantage of the presented thesis is that their major parts were already published in scientific journals. The papers were peer reviewed and therefore the scientific and technical quality of the thesis result was already positively evaluated.

The thesis is good and meets all criteria to be taken to the defence.

Miroslav Černík

In Liberec (Czech R.) on October 30, 2017 **Prof. Dr. Ing. Miroslav Černík,CSc.**