International Journal of Engineering Research And Management (IJERM)
ISSN: 2349- 2058, Volume-05, Issue-07, July 2018

Novel Low Cost Adsorbent for the Removal of Rhodamine B Dye from Wastewater

Shweta Mitra, Tirthankar Mukherjee

***Abstract*— This study deals with the preparation of Activated Carbon (AC) from spent tea leaves collected from local shops and stalls. 5% NaOH solution was used to chemically activate the tea leaves in a ratio of 1.5:1 (NaOH: Carbonized tea). The activated tea leaves were further subjected to carbonization at 350°C for 2hrs. The prepared AC was impregnated with iron nano-particles (TAC/Fe). This TAC/Fe was used to adsorb Rhodamine B dye aqueous solution. The effect of different parameters such as pH, adsorbent dosage (g/l), the initial concentration of dye (ppm) and temperature (°C) were studied. The removal % decreases as the initial dye concentration increases and with increase in pH it also decreases as obtained from the effects of the individual parameters. The removal of RB dye increases with the increase in adsorbent dosage. From the thermodynamic study it has been observed that at a low temperature of 30°C the molecular motion was very low and the removal efficiency was 85.25 % but at higher temperatures around 80-100°C, the removal efficiency increased to 90.2%.**

***Index Terms*— Spent tea leaves; Chemical Activation; Activated Carbon; temperature**

I. INTRODUCTION

The environment has sustained negative impacts since the advent of industrialization. Application of dyes on major note can be seen in industries like leather, food, textile, and paper. An estimate of 700000 tons of dyes is produced each year out of which around 2 % is reported to make it to the environment and hamper the balance of the ecosystem [1]. These effluents that are carrying contaminants in the form of dyes must be treated to accepted standards from the different industries before their release into the ecosystem. Rhodamine B (RB) is a dye encountered very frequently in the textile industry for the purpose of dyeing wool, silk, and cotton. RB upon contact with eyes causes a highly irritable sensation and a feeling resembling burning may be felt as well which may lead to severe damage to the eyes of both animals and humans leading to permanent damage [2].

Methods of treating wastewater have been an ongoing research and many methods have been tried for the successful removal of impurities present in wastewater. Some methods to have been applied include coagulation, reverse osmosis, photo-degradation, chemical oxidation, membrane filtration methods, ozonation, and biosorption [3]. Although the aforementioned process may be suitable in many cases but for dye removal either the methods are inefficient or have abnormally high costs which prevent their acceptance on a larger scale. Adsorption provides an alternative to these methods and is found suitable for the purpose of dye removal from wastewater. The suitability of activated carbon for these processes remains unchallenged due to added advantages of operation over high temperature, a wide range of pH, easy separation and an enormous porosity which helps it in adsorbing large amounts of impurities [4]. One of the most popular methods of modifying activated carbons is to make a metal oxide-activated carbon composite which provides added enhanced desirable characteristic of porosity having the advantage of greater control in terms of pore structure and surface functional groups thus altering its adsorption properties. Extensive reports of literature can be noted where metal oxides such as aluminum oxide, iron oxide, zinc oxide, manganese oxide, copper oxide and vanadium oxide have been used to modify the properties of activated carbons [5-6]. These metal oxides are impregnated in the activated carbon matrix to enhance its adsorption capacity or to make a noticeable improvement in its ability in bringing about catalytic oxidation for dye wastewater.

The precursor for the production of activated carbon plays a huge role in its quality as an adsorbent. Many agro-related wastes have been in use as a precursor for the production of activated carbon like agricultural waste, wood, leaves, baggase, various seeds etc [7]. One of most low-cost beverage tea is perhaps the oldest and most widely consumed beverage in the world after water. With more than 2000 various variants of tea available for consumption in the global market, it is regarded as one of the major contributors to the world beverage market. India known traditionally for its different authentic varieties of tea is also one of the leading producers and consumers of tea in the global market [7]. Spent tea leaves which are a waste product of industrial and domestic importance can serve as a source of activated carbon as the carbon content of 30% can be noted in spent tea leaves [8]. With proper physical and chemical activation, this potential could be tapped into and design of low-cost adsorbent could happen that would have the ability to remove various dyes from their aqueous solution.

In this study activated carbon was prepared from spent tea leaves collected collected from local shops and stalls. 5% NaOH solution was used to chemically activate the tea leaves in a ratio of 1.5:1 (NaOH: Carbonized tea). The activated tea leaves were further subjected to carbonization at 350°C for 2hrs. The prepared AC was impregnated with iron nano-particles (TAC/Fe). This TAC/Fe was used to adsorb Rhodamine B dye aqueous solution. The effect of different

Manuscript received July 22, 2018

Shweta Mitra, Department of Chemical Engineering, Jadavpur University, Kolkata, India

Tirthankar Mukherjee, Department of Chemical Engineering, Jadavpur University, Kolkata, India

parameters such as pH, adsorbent dosage (g/l), the initial concentration of dye (ppm) and temperature (°C) were studied.

II. MATERIALS AND METHODS

A. Chemicals

All chemical reagents were of analytical grade and were used without further purification. Spent tea leaves were collected from the local market and were washed thoroughly before use. Iron Sulphate Heptahydrate (Fe_2SO_4, $7H_2O$) used for iron impregnation was purchased from Merck, India. Rhodamine B was obtained from SRL Chemicals. Hydrochloric acid (HCl), 37%, and sodium hydroxide (NaOH) required for monitoring the pH was also purchased from Merck.

B. Preparation Activated Carbon from spent tea leaves (TAC)

Spent tea leaves were collected from the local shops and stalls. Then it was repeatedly washed to remove dirt and loose soil particles. Afterward, it was dried for 48 hours at 80°C in a hot air oven (Make: Spac n Services). The dried mass was carbonized at 450°C for 2 hours in a muffle furnace (Make: Spac n Services). The carbonized tea was sieved with a 250µm mesh and fine particles were obtained which was subjected to chemical treatment with 5% NaOH. The NaOH solution was added to the carbonized tea leaves in a ratio of 1.5:1. The mixture was kept for 12 hours for the activation. After the process was complete the mixture was washed repeatedly until it became neutral. The partially activated carbon was then dried in a hot air oven for 24 hours. The dried material was put into the muffle furnace for further carbonization at 800°C for 2 hours.

C. Preparation of iron impregnation in TAC (TAC/Fe)

A weighed amount of the prepared AC was blended with iron salt (Fe_2SO_4, $7H_2O$) in a solution of 1:5 (w/w) ratio. The formed mixture was stirred in a magnetic stirrer (Make: Remi) and heated to 100°C for 2 hours while 10% NaOH solution was added dropwise for 5 min to precipitate the hydrated iron oxides. The final product (TAC/Fe) was repeatedly washed with water until its pH became neutral. The final product was dried and kept for further use.

D. Characterizations

To find the surface topographical characterization of the prepared activated carbon Scanning Electron Microscope (FEI INSPECT F50 FESEM) consisting of Tungsten filament was employed for the surface characterization. The scan settings were set at an accelerator voltage of 10 kV and an emission current of 100mA˚. Furthermore, the physicochemical characterization was obtained via XRD spectroscopy (Rigaku Ultima III). The copper filament was used with 40kV and 30mA.

E. Experimental procedure

All the adsorption experiments were carried out in batch mode. 200 ml of aqueous solution of RB dye was taken in a flask for each of the experiments. The flask was placed on a temperature controlled magnetic stirrer. A known amount of activated carbon was added and the stirrer was started immediately. Same stirring speed (300 rpm) was maintained for all the experiments. The experiments were conducted with different initial concentrations of the dye solution. Initial pH of the solution was maintained by adding 0.1M HCl and 0.1M NaOH solution before adding the activated carbon. After a certain fixed time of adsorption, the solution was filtered. The final RB solution concentration was measured using UV-Visible Spectrophotometer (Perkin Elmer UV/VIS Lambda 365) at a wavelength of 554nm. The percentage removal of dye was calculated using the following equation:

$$\text{Removal Efficiency} = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f are the initial and final concentrations of RB solution, respectively

III. RESULT AND DISCUSSION

A. Characterization

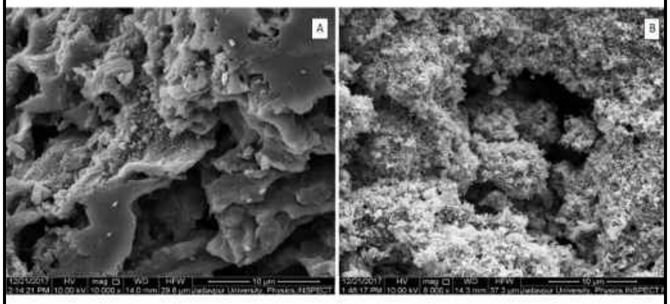

Figure 1: SEM images of (A) Activated Carbon (B) TAC/Fe

Fig. 1 depicts the morphological characteristics of TAC/Fe material obtained from SEM images. Fig. 1A and Fig. 1B depicts the structure at 10µm magnification. It can be seen with distinct clarity that the surface morphology of the activated carbon has been modified by a deposition of iron particles. Visibility of pores can be deemed distinct encircling which the iron at different states of oxidation can be seen to be present. It can also be concluded that the pores obtained are micropores.

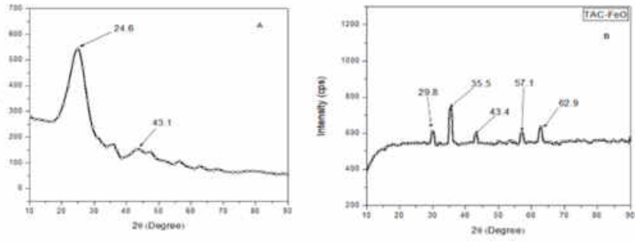

Figure 2: XRD image of (A) Activated Carbon (B) TAC/Fe showing the peaks of Fe

Fig. 2A shows the XRD profile of the neat AC produced from spent tea leaves. The prepared activated carbon exhibits a very broad band of diffraction peaks along with the absence of sharp peaks which indicated that it is predominantly an amorphous structure. There are two broad diffraction peaks around 2θ = 24.6° and 43.1° in the spectrum, corresponding to the diffraction of (0 0 2) and (1 0 0), respectively.

Fig. 2B shows the XRD patterns as obtained for TAC/Fe.

Two crystalline phases can be distinctly determined from the XRD pattern. The two characteristic crystalline phases are of magnetite and hematite. Magnetite is an oxidized crystal form of iron with an inverse spinel type cubic structure having two active sites that are not equivalent in symmetry. The two nonequivalent structures being tetrahedral and octahedral while hematite being a crystalline solid of the hexagonal compact structure. 29.8, 35.5, 43.4, 57.1 and 62.9 are the intensities obtained at 2θ values. Furthermore, a higher degree of crystallinity is observed at the magnetite portion of the material. It may be worth mentioning here about another member of the iron oxide family namely maghemite, comprising of cubic structure of inverse spinel type having a similar structure to that of magnetite only differing in the fact that exclusively contains Fe(III) oxide. Similarly in the structure of maghemite and magnetite makes it very difficult for the distinct identification of one from the other using XRD alone as a characterization method.

B. Effect of Different Parameters on the removal efficiency of Rhodamine B using TAC/Fe

B.1. Effect of pH on the removal efficiency of Rhodamine B

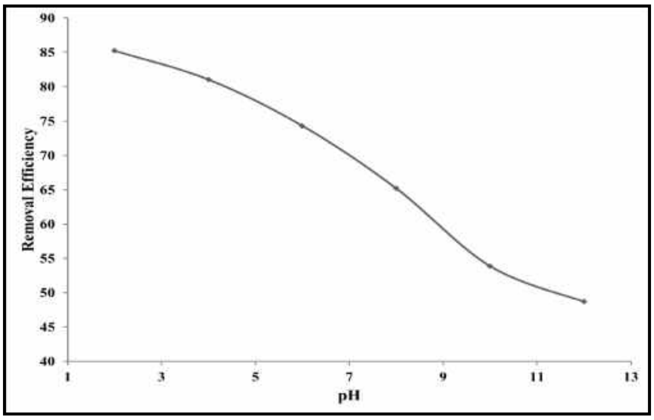

Figure 3: Removal Efficiency of Rhodamine B at different pH values. Initial Dye Concentration: 10ppm, Adsorbent Dosage: 0.5g/l, Temperature: 30°C, Time: 16 hours

The pH of wastewater solution is considered by far on the greatest factors that have an extremely significant effect on the process of adsorption during impurity removal and has been considered perhaps the most important parameter in determining optimum conditions for the removal of dyes from water solutions. pH plays such a huge role in the adsorption process majorly because of its contribution towards controlling the surface charge of the adsorbent. This basically has a pronounced effect on the electrostatic interaction between adsorbent and adsorbate which plays a role in the dissociation and association of the adsorbate molecules on the active sites. Figure 3 depicts the effect of pH on the removal efficiency of the prepared adsorbent with respect to RB removal. As the figure depicts pH had a pronounced effect on the removal of the dye from the aqueous solution. The removal efficiency was seen to be slightly increased in the range of 1-3 pH. Removal percentage was seen to attain a highest of 85.25% at 2 pH while a contrasting removal percentage of only 48.7% was noted at 12 pH. Removal percentage was seen to be progressively decreased as the pH increased towards a more basic zone. Removal efficiency attained a maximum at a pH of 2 in the current study. Similar trends have been noted in other studies of RB removal where a lower pH has been preferred for the adsorption study. RB removal using pine needles being one such example. RB at pH lower than 4 tends to exist as a cationic monomer while at greater pH RB tends to exist in zwitterion form. The zwitterions have a dimeric nature thus being a lot greater in size are not easily absorbed into the porous structure of the activated carbon while at the same time the much smaller cationic monomer has an easy access to the active sites of the activated carbon [9]. Thus all the experiments for RB removal in the current study were conducted at pH 2

B.2. Effect of Adsorbent Dosage on the removal efficiency of Rhodamine B

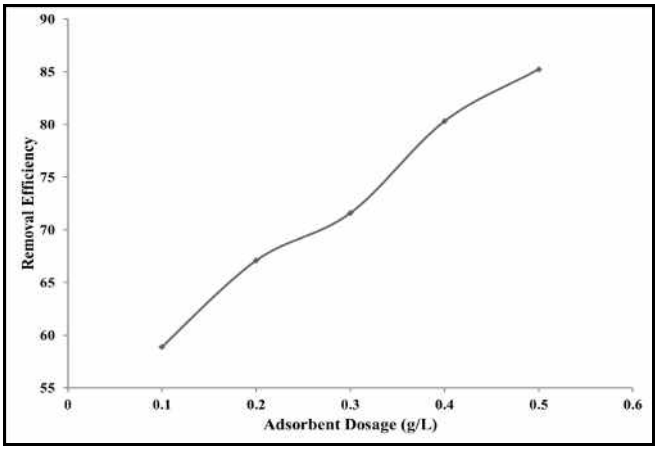

Figure 4: Removal Efficiency of Rhodamine B at different Adsorbent Dosage (g/l). Initial Dye Concentration: 10ppm, Temperature: 30°C, Time: 40 mins., pH: 2

The adsorbent dosage varied from 0.1 – 0.5 g/L. From Figure 4. it is evident that there was a steady increase in the removal of RB as the amount of adsorbent dosage increased. This is due to the fact that with the increase in dosage the number of free pores and surface area increased greatly and thus adsorption increased resulting in higher removal efficiency. This is probably due to the conglomeration of adsorbent particles which results in no further increase in surface area of the AC [10]. Thus the removal efficiency becomes almost constant. Highest removal efficiency of 85.25 % was observed at 0.5g/L and the least of 58.9 % was found at 0.1g/L.

B.3. Effect of Initial Dye Concentration on the removal efficiency of Rhodamine B

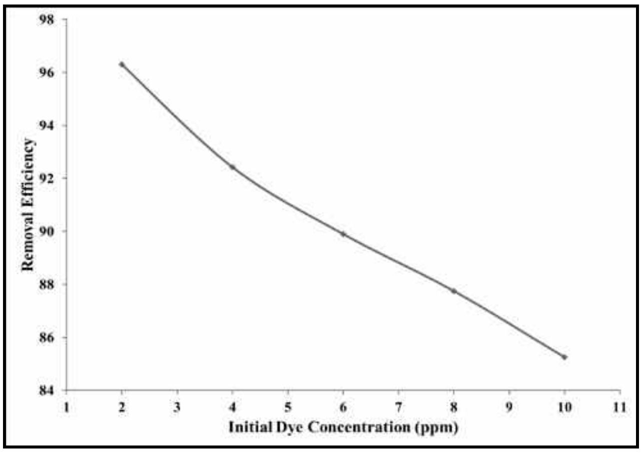

Figure 5: Removal Efficiency of Rhodamine B at different Initial Dye Concentration (ppm). Adsorbent Dosage: 0.5g/l, Temperature: 30°C, Time: 40 mins., pH: 2

An initial concentration range of 2ppm – 10ppm was taken where absorption onto TAC/Fe was carried out. From Fig. 5 we can see that the removal efficiency has a steady decrease trend as the concentration of the dye increases. At low concentrations, there will be unoccupied active sites on the adsorbent surface. Initially, the removal percentage was 96.3% due to the presence of abundant free pores but as the concentration increased the pores become blocked and the removal efficiency decreased. The highest removal efficiency was 96.3% at 2ppm and least was 85.25% at a 10ppm concentration of RB solution.

B.4. Effect of Temperature on the removal efficiency of Rhodamine B

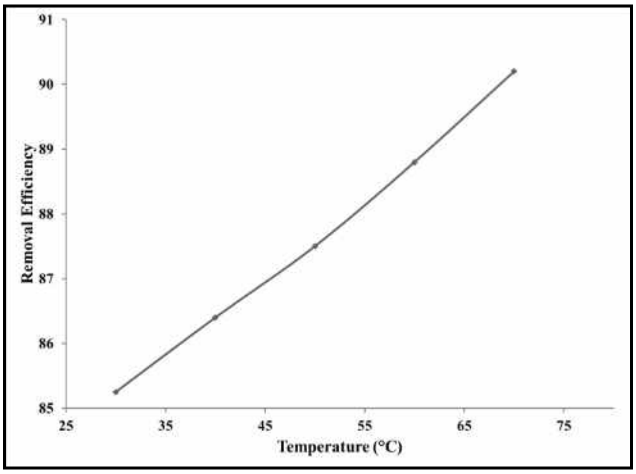

Figure 6: Removal Efficiency of Rhodamine B at different Temperatures (°C). Initial Dye Concentration: 10ppm, Adsorbent Dosage: 0.5g/l, Time: 40 mins., pH: 2

From Fig. 6 it is evident that with the rise in temperature there has been a continuous increase in the removal efficiency of the dye. Increase in temperature results in random motion of fluid particles. The intermolecular distance increases and there is a constant rapid motion of the molecules. Due to this, as the temperature rises the RB molecules start to vibrate rapidly and their probability of getting absorbed into the TAC/Fe pore increases [11]. At a low temperature of 30°C the molecular motion was very low and the removal efficiency was 85.25 % but at higher temperatures around 80-100°C, the removal efficiency increased to 90.2%. The thermodynamic parameters that are evaluated are the changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°). The ΔH° and ΔS° are determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Whereas ΔG° is confirmed using the following equation:

$$\Delta G^\circ = -RT \ln K$$

Where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature and K is the equilibrium constant. The slope and encounter of the plot of ln K vs 1/T resulted within the values of ΔH° and ΔS°, respectively. The calculated values of ΔH°, ΔS°, and ΔG° are given in Table 2. A negative worth of ΔG° suggests the viability and spontaneous nature of the surface assimilation method with a high preference of RB onto the TAC/Fe. A positive worth of ΔH° indicates the energy-absorbing nature of the surface assimilation method. The low values of each ΔG° (20 to 0 kJ/mol) and ΔH° correspond to physical surface assimilation. A positive worth of ΔS° reflects the inflated randomness at the solid-aqueous interface with some structural changes in adsorbate and adsorbent.

Temp. (K)	$\Delta G^\circ\ KJ/mol$	$\Delta H^\circ\ KJ/mol$	$\Delta S^\circ\ J/molK$
303	-10.5755	0.004988	0.034919
313	-10.9247		
323	-11.2738		
333	-11.623		
343	-11.9722		

Table 1: Thermodynamic parameters for adsorption of RB onto TAC/Fe Initial Dye Concentration: 10ppm, Adsorbent Dosage: 0.5g/l, Time: 40 mins. , pH: 2

B.5. Effect of Time on the removal efficiency of Rhodamine B

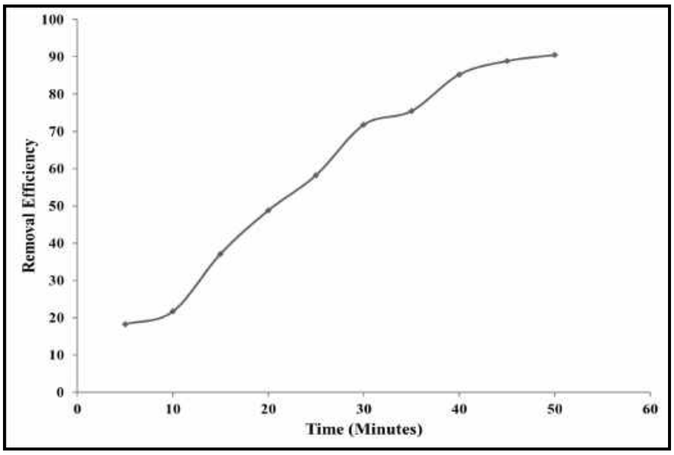

Figure 7: Removal Efficiency of Rhodamine B at different Time (min.). Initial Dye Concentration: 10ppm, Adsorbent Dosage: 0.5g/l, Temperature: 30°C., pH: 2

A 50-minute time range was taken where the removal % of RB solution onto TAC/Fe was studied. From the figure 7. it is evident that there is a continuous increase in the removal efficiency with time. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites are vacant and a solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in a number of vacant sites of adsorbent and dye concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of RB on the adsorbent surface. This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium.

CONCLUSION

From the above study we can conclude that pH, Initial Dye Concentration (ppm), Dosage (g/L) and Temperature (°C) play a significant role in adsorption of RB using TAC/Fe. The removal % decreases as the initial dye concentration increases and with increase in pH it also decreases as obtained from the effects of the individual parameters. The removal of RB dye increases with the increase in adsorbent dosage. From the thermodynamic study it has been observed that at a low temperature of 30°C the molecular motion was very low and the removal efficiency was 85.25 % but at higher temperatures around 80-100°C, the removal efficiency increased to 90.2%.

REFERENCES

[1] Lavecchia R., Pugliese A., Zuorro A., (2010) Removal of lead from aqueous solutions by spent tea leaves, Chemical Engineering Transactions, 19, 73–78.
[2] Demirbas A., (2008) Heavy metal adsorption onto agro-based waste materials: A review, J. Hazard. Mater, 157, 220–229.
[3] Hameed B.H., (2009) Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard. Mat, 161, 753–759.
[4] Zuorro A., Lavecchia R., (2010) Adsorption of Pb(II) on spent leaves of green and black tea, Am. J. Appl. Sci., 7, 153–159.
[5] Amarasinghe BMWPK and Williams A.R., (2007) Tea Waste As a Low Cost Adsorbent for the Removal of Cu and Pb, from Waste Water, Chem. Eng. J, 132, 299-309.
[6] Jun T.Y, Arumugam S.D, Latip N.H.A, Abdulla A. M and Latif P. A, (2010) Effect of Activation Temperature and Heating Duration on Physical Characteristics of Activated Carbon Prepared from Agriculture Waste, Environment Asia3 (special issue),143-148.
[7] Hameed, B.H., Din, A.T.M., Ahmad, A.L., (2007) Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. J. Hazard. Mater. 141, 819–825.
[8] Hema, M., Arivoli, S., (2008) Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon. J. Appl. Sci. Environ. Manage. 12 (March (1), 43–51.
[9] Jonusas A, Miknius L. (2014) Effect of the pressure and feedstock state on the yield and properties of waste tire thermolysis products. Energy Fuels; 28: 2465–71.
[10] Diez C, Martinez O, Calvo LF, Cara J, Morán A. (2004) Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered. Waste Manag; 24:463–9.
[11] Tay, T., Ucar, S., Karag€oz, S., (2009). Preparation and characterization of activated carbon from waste biomass. J. Hazard. Mater. 165, 481-485.