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Production of activated carbon from spent tea and its application in the treatment of textile dyes

Arooj Azhar*, Shahnaz Choudhry

Department of Biotechnology, Kinnaird College for Women, Lahore, Pakistan

Abstract

Activated carbon (AC) being a high-quality adsorbent can be produced from agricultural wastes that are economical in comparison to several carbonaceous raw materials and commercially available carbons for water purification. Here, AC was produced from washed, sun and oven dried spent tea after digestion with 0.5M and 1 M potassium acetate used as an activating agent, direct combustion, and carbonization in muffle furnace at 500°C. Later, the sorbent was sieved through 250μm and 560μm mesh sizes and was characterized for pH, ash content, iodine number, moisture content, and percentage yield. The effect of sorbent size, sorbent dosages and contact time on adsorption ability of AC to remove methylene blue (cationic dye) and reactive red 120 (anionic dye) from textile industrial effluent was studied. The maximum yield was 31.41% from 100g of the bio-sorbent. Maximum adsorption ability of activated carbon produced from 1M treated spent tea relates with high iodine number, 422.8mg/g. The AC with alkaline pH led to higher percentage removal of cationic dye (99.71%) as compared to the anionic dye (38.57%) at sorbent dose (0.3g/ml), sorbent size (250μm) and contact time (2.5h). The current findings helped in understanding the efficacy of AC at two wavelengths, 668nm and 536nm for methylene blue and reactive red, respectively for dye removal from industrial wastes. Additionally, this cost-effective method can be utilized on large scale to treat wastewater and lessen the environmental pollution to a safe extent.

*Corresponding Author: Arooj Azhar ✉ azhar_arooj@yahoo.com

Introduction

Activated carbon (AC) or activated charcoal belonging to the class of non-graphitizing carbon is known as a very good adsorbent due to large surface area of its particles, micro porous structure, and high surface reactivity. AC is formed using various carbonaceous sources of raw materials similar to coal, tires, peat and commercially prepared carbons which are expensive precursors for its preparation (Peter *et al.,* 2008). Due to emerging demand, various commercial strategies were developed for using agricultural wastes as precursors for AC. The production of activated charcoal from various agricultural wastes has been reviewed over the years (Ioannidou and Zabaniotou, 2007; Ahmaruzzaman and Gupta, 2011; Kouotou *et al.,* 2013; Igwegbe *et al.,* 2016). The uses and characteristics of ACs produced from agricultural wastes and those commercially prepared were compared. The adsorbent power of the AC varies on the basis of pore size which increases on their treatment with diverse activating agents making them more efficient adsorbent by expanding the pores of the particles. The estimated surface area of the carbon after its carbonization and activation is $1500m^2/g$ which depicts the massive adsorbent activity of the AC (Peter *et al.,* 2008; Kumar *et al.,* 2013).

Activating agents like various acids HCl, H_2SO_4, H_3PO_4 and certain alkaline agents NaOH, KOH, $ZnCl_2$, CH_3COOK and CO_2 can be treated with different carbonized precursors for making the carbonaceous material active (Haque, 2020; Yagmur *et al.,* 2020). High sorbent aptitude and surface reactivity makes activated charcoal more effective in wastewater purification, heavy metals removal, and decolourization of hazardous textile dyes nowadays (Ioannidou and Zabaniotou, 2007; Demirbas, 2009). Various forms of biological by-products and agricultural biomasses are available in Pakistan and all over the world which can be utilized for AC production and their application in the treatment of impurities due to the functional groups like hydroxyl, carboxyl and amino groups present on their surface

giving them very efficient sorbent properties (Bhatti *et al.,* 2015).

Raw materials can be activated by either physical or chemical activation process. Former process involves separate steps of activation and carbonization. Chemical activation includes simultaneous carbonization and activation steps. Various chemical activating agents are exploited prior to carbonization for impregnation of the raw material. Temperatures employed for carbonization in chemical activation are usually lower than those for physical activation, making it a more resourceful method (Rajeshwar *et al.,* 2012).

In the past few years, different techniques have been in use for the treatment of wastewater generated from industrial sector which include flocculation, membrane filtration, chemical activation, photo-catalysis, adsorption and electro dialysis. Of all these, liquid phase adsorption procedure was considered most effectual and proficient for removal of dyes, heavy metals and obstinate compounds from wastewaters. Adsorption process makes use of adherence of adsorbate on the surface of solid adsorbent (Amey and Ganvir, 2013; Shawal *et al.,* 2014; Garba *et al.,* 2015). AC prepared from tea waste using potassium acetate as an activating agent resulted in 97.88% adsorption of the dye acid blue 25 (Auta and Hameed, 2007). In another research AC was prepared from coconut shells using potassium acetate, potassium hydroxide and CO_2 as a chemical activating agent. Potassium acetate showed more adsorbent capacity than other activating chemicals (Shawal *et al.,* 2014).

Tea waste is an easily available raw material for AC production and its employment in treatment of wastewater. Apart from spent tea, various other agricultural waste precursors for production of activated charcoal include rice husk, egg shell wastes, sugarcane bagasse, orange fruit peel, jack fruit peel, coconut shells, cocoa pods, hazel nut husks, walnut shells, peanut shell and sawdust. The enormous amount of carbon in these raw materials makes them effective, which after treatment with specific activating agents or carbonization at elevated

temperatures produce carbon in activated form (Imamoglu and Tekir, 2008; Ahmaruzzaman and Gayatri, 2010; Guijarro-Aldaco *et al.,* 2011; Zuorro *et al.,* 2013; Yang *et al.,* 2019; Liu *et al.,* 2020). These precursors produce AC with very high adsorption capability which makes it effective in removal of heavy metals like lead, cadmium, mercury, arsenic and copper from the industrial effluents and sewage disposals (Prahas *et al.,* 2008; Kanawade *et al.,* 2010; Liu *et al.,* 2020). Textile industrial dyes are composed of azo, cationic and certain anionic dyes which are also playing their role in increasing environmental pollution. These hazardous dyes can be treated using activated charcoal prepared from spent tea for their elimination from water (Rao *et al.,* 2004; Hameed, 2009; Uddin *et al.,* 2009).

The chemical activation of the carbonaceous spent tea using potassium acetate is very effective in expansion of its porous surface area which elevates the adsorbent nature of the activated carbon. Its high surface reactivity helps in very efficient amputation of azo dyes and basic dyes from wastewater of textile industries (Uddin *et al.,* 2009; Rafatullah *et al.,* 2010). These dyeing agents used in textile industries are heavily polluting the water and are distressing the dissolved oxygen demand of the water bodies, therefore need to be treated. In export sector of Pakistan, textile industries play a crucial role. Wide range of processes starting from production of fibre to final finishing of the product is carried out in textile industries utilizing water, surfactants, dyes and other chemicals. Due to the fact, the wastewater of textile industries is highly contaminated contributing to high amount of chemical oxygen demand, dissolved and suspended solids, biological oxygen demand, heat and colour. This is the reason for treating textile wastewater past its discharge (Bhatti *et al.,* 2015; Garba *et al.,* 2015). Due to the great threat to water bodies and vast availability of agricultural waste products, this study simultaneously utilized spent tea AC for the confiscation of colours from textile wastewater, and measuring BOD_5, COD and pH.

National Environmental Quality Standards (NEQs) Pakistan has set a specific range and limit of the factors like BOD_5, COD, temperature, chlorides, phosphates, alkalinity, turbidity, suspended solids, dissolved solids and pH of the discharged wastewater. If the range of these parameters exceeds the set range than it leaves harmful and perilous effects on the water bodies, against law and is a cause for the increment of pollution. Therefore, it is essential step for nearly all the textile industries to check these parameters before discharging their wastes. Current situation of most of the textile factories in Pakistan release their effluents without proper treatment, hence, adding to the environmental pollution (Haydar and Bari, 2011).

Dyes in textile effluents mainly include cationic, basic, heterocyclic aromatic dyes like methylene blue and malachite green and anionic dyes like reactive blue 19, blue 21 and azo dyes like cibacron yellow, congo red and reactive red 120 (Tahir *et al.,* 2009; Bijari and Younesi, 2019; Wong *et al.,* 2020; Said *et al.,* 2020). Synthesis of these dyes utilizes very harmful chemicals which can affect reproduction process in humans and can be carcinogenic for the offspring of animals exposed to these aromatic amines during gestation period (Auta, 2012; Radaei *et al.,* 2014).

AC being a very effectual sorbent is usually sieved for the maintenance of even sized particles because optimization of particle size with the elimination of oversized and undersized particles is very important. The mesh sizes which are best in context to the sorption activity are usually ranging from 40μm to 500μm. The low mesh size sieving tends to yield charcoal with little pore size and greater surface area, thus increasing the sorption phenomenon. Whereas large mesh size particles tend to hinder the sorption process as the pore sizes are not well exposed, leading to the poor sorption quality. The removal efficiency of the dyes is increased with decrease in the particle size, owing to the fact that more surface area at smaller particle size provides more sites for sorption process (Thirumalisamy and Subbian, 2010; Rahman *et al.,* 2012).

The sorbent prepared from agricultural biomasses can be characterized for moisture content, ash content, iodine number, pH, methylene blue number, percentage yield, BET surface area, chlorine half length, molasses number and isotherms. Iodine number directly indicates the adsorption tendency at micro porous level. More iodine number is an indication of high adsorption aptitude (Rajeshwar *et al.,* 2012; Majedi *et al.,* 2014). AC produced using spent tea was utilized in the current study for the evacuation of colour from the textile industrial wastewater. The adsorption activity of AC on dyes can be checked by studying contact time of sorbent with the dye molecule surface, at varying temperatures, varying dosage of sorbent by keeping the volume of effluent constant. The following parameters like shaking speed, temperature and contact time, effect of sorbent and effluent concentration affect the adsorption process during application of dyes removal (Thirumalisamy and Subbian, 2010; Radaei *et al.,* 2014; Bhatti *et al.,* 2015). The purpose of this study was to produce AC on laboratory scale from spent tea by using potassium acetate as an activating agent and to check its adsorption capability for removal of textile industrial dyes through a cost effective and eco-friendly method.

Materials and methods

Sample Collection

The samples of spent tea were collected from houses and various tea stalls in Lahore in green produce bags that helped to absorb the ethylene gas generated by the green plants by the zeolite mineral "Oya" in them. These specific produce bags used for sampling helped in prevention of foul odour, rottening and maintaining the sample quality.

Production of Activated Carbon

Washing and Drying of the Sample

Spent tea sample was given 10-12 washings with tap water using tea strainers and sieves to remove all the residual leftovers of milk and traces of any flavouring agents. The properly washed tea sample was then dried in sunlight consecutively for 10 days to remove the moisture content of the sample. The sun-dried sample was further oven dried in order to remove any content of the moisture left. The spent tea samples were placed in troughs and were dried at 60°C for 34 hours. Weight of the samples at each step was measured using electronic balance (Shimadzu, Mettler Toledo Company).

Digestion with Potassium Acetate

Two molarities, 0.5M and 1M of potassium acetate (Riedal- De Haen Company) buffers were used for the digestion procedure to produce AC from spent tea. The digestion process was done twice, first with 50g and then with 200g of the oven dried sample to check for reproducibility of results. 50g sample was taken and digestion procedure was carried out with two molarities potassium acetate buffers in 1:1 ratio. 25ml of 0.5M and 1M potassium acetate was added to 25g of spent tea sample separately in a beaker and stirred mechanically to ensure proper mixing. Similarly, 100g of sample was digested in 1:1 ratio for both the concentrations. Samples were then covered with aluminium foil and kept in dry oven (Memmert Instruments) for 24 hours at 40°C.

After 24 hours of digestion, almost 12-15 washings were given with distilled water to properly remove the leftovers of the buffer. During washing, pH was measured with pH meter (InoLab Instruments) and adjusted to neutral with NaOH (Riedal-De Haen). The neutral pH indicates that there is no buffer residue present in the sample. Washing was again done after addition of NaOH and pH adjustment. Samples were weighed.

Direct Combustion and Carbonization

Direct combustion generates the residual carbon left after burning. Sample was taken in small amounts in china dishes and burnt directly on Bunsen burner. Carbonization was done at 500°C for production of AC from the carbonaceous ash generated after direct combustion. Samples were placed in porcelain crucibles and kept in muffle furnace (Nabertherm) for 15 minutes at 500°C. This generates the AC. After gradual cooling, samples were taken out of the furnace and sieved

using soil sieve shaker (Octagon Digital Company) with 250μm and 560μm mesh sieves, eliminating all the oversized and undersized particles.

The AC produced was stored in airtight PET (Polyethylene Tetraphthalate) packets in order to prevent any moisture from affecting its quality.

Characterization of Activated Carbon Produced

To 1g of AC of both molarities, distilled water was added and mixed on magnetic stirrer (Bante Instruments) for 1 hour. Solution was allowed to stabilize for 5 minutes and pH was determined (Ioannidou and Zabaniotou, 2010).

The porcelain crucibles were taken and pre weighed, 1g activated carbon was added and accurately weighed. The porcelain crucibles were kept in muffle furnace at 500ºC. Next day, crucibles were taken out and weighed again.

Ash content was calculated by the formula:

$$\text{Ash content (g)} = \frac{\text{Weight of Ash (g)}}{\text{Weight of Oven Dried Precursor (g)}} \times 100$$

Iodine number is one of the tests to evaluate the adsorption activity. The more the value of iodine number in mg/g, greater is the surface quality of the AC. Iodine number test was performed in two steps.

Standardization of Activated Carbon

10ml of 0.1N iodine standard solution was taken in Erlenmeyer flask to which few drops of 1% starch indicator (Sigma Aldrich, Riedal-De Haen) were added generating blue coloration. It was titrated against 0.05N Sodium Thiosulphate (Riedal-De Haen) solution until it became colourless. The reading on the burette was noted and taken as Blank Reading (B).

Titration with Activated Carbon

0.2g of AC of each molarity was taken in Erlenmeyer flask to which 40ml of 0.1N iodine solution was added, stirred for 5 minutes and filtered using Whatman filter paper. To 10ml filtrate of both molarities 2-4 drops of 1% starch were added as an indicator. The solution was titrated against 0.05N Sodium Thiosulphate until it became colourless. Three concordant readings were taken and considered as titration reading (A).

Iodine number was calculated as,

Iodine number = Conversion factor (mg/g) x C

Conversion factor and C were calculated as follows:

$$\text{Conversion factor} = \frac{\text{Normality of iodine x Molecular weight of iodine (g)}}{\text{Blank reading x Weight of carbon (g)}} \times 40$$

C= B-A

The moisture content of AC was determined by placing 1g AC of 0.5 and 1 M concentration in pre-weighed porcelain crucibles kept in dry oven for 4 hours at 105ºC. Samples were taken out. The moisture content was calculated as:

$$\text{Moisture content (\%)} = \frac{\text{Weight loss after drying (g)}}{\text{Initial weight (g)}} \times 100$$

Percentage yield of AC produced for two molarities (0.5 M and 1.0 M) was calculated by the formula:

$$\text{Percentage yield (\%)} = \frac{\text{Weight in grams of Activated carbon produced (g)}}{\text{Weight of dried raw material used in grams (g)}} \times 100$$

Application of Activated Carbon in the Textile Wastewater Treatment

The textile industrial wastewater was collected from Lahore in plastic bottles one day prior to its treatment and was stored in refrigerator.

Wastewater Quality Parameters

Textile wastewater pH was checked before and after treatment with activated carbon. Biological oxygen demands of the textile industrial wastewater were checked using DO (Dissolved Oxygen) Meter, Jenway. BOD_5 test was performed by taking 5ml of unheated control and AC filtered textile wastewater in brown incubation bottles. To these, 300ml of distilled water was added and initial reading was taken. Samples were placed in dark in incubator for five days at 20ºC and readings were again taken to calculate BOD_5 (Igwegbe *et al.,* 2016). Chemical oxygen demand of the untreated and treated textile effluent was calculated using COD meter (Lovibond RD125). Solution of potassium dichromate and 85% sulphuric acid were added in COD vial, to which 2ml textile wastewater was added.

It was then placed for 2 hours at 150°C in COD calibrator. After two hours, readings were noted.

Dye Removal

The method used for removal of dyes was according to (Kumar *et al.,* 2013). Four sets of five test tubes, each with one for negative control containing textile wastewater were prepared. The test tubes were labelled according to the varying dosages of the sorbent, pore size and concentration of AC used. 15ml of the textile wastewater was added in all of the test tubes. Samples were then placed in shaking incubator (Memmert) at 150rpm speed and 45°C for different time durations to check the effect of contact time on adsorbent activity of AC produced. The influence of sorbent dosage on dye removal efficiency was checked by altering the amount of the sorbent doses as, 0.1, 0.15, 0.2, 0.25 and 0.3g. The volume of the industrial effluent used remained constant. The relationship between removal of dyes and contact time with the biosorbent was studied. This was done by placing the samples in the shaking incubator for 30, 60, 90, 120 and 150 min. This was done to check the effect of time on the activity of the biosorbent and its counter role in removal of the dyes from the textile industry wastewater. The effect of the pore size on adsorption of dyes from the textile wastewater was checked by using AC of two different pore sizes, 250 and 560µm.

When the required time was achieved the samples were taken out of the shaking incubator and filtered.

The filtrate was evaluated for the percentage of dyes adsorbed by the activated charcoal. The absorbance of two dyes, methylene blue and reactive red 120 was taken using UV/Vis spectrophotometer (Analytik Jena, Specord 200 Plus) at 668nm and 536nm wavelengths, respectively.

The following formula was applied to check percentage removal,

$$\% \text{ age Dye Removal} = \frac{\text{Initial Absorbance} - \text{Final Absorbance}}{\text{Initial Absorbance}} \times 100$$

Results

Weight of Spent Tea Sample

Initial wet weight of spent tea sample was 1222.25g. After sun drying weight was reduced to 273.87g. The final weight obtained after oven drying was 258.58g with the removal of moisture content of 78.86%.

Activated Carbon

The activated carbon produced for both the molarities indicated that there is four folds increase in the weight in 25g and 100g samples. The maximum value was obtained with 1M concentration of activating agent after digestion, direct combustion and carbonization (Table 1). Activated charcoal sieved using two mesh sizes 560µm and 250µm showed maximum adsorption capability of more fine particles (Fig. 1).

**Table 1.** Production of activated carbon from spent tea.

Molarity of CH$_3$COOK	Amount of Sample (g)	Weight after Digestion (g)	Weight after Direct Combustion (g)	Weight after Carbonization (AC Weight) (g)	Weight of AC after Sieving (g)		Total Weight Loss (g)
					560µm	250µm	
0.5M	25	77.46	14.04	5.46	3.81	1.05	19.54
	100	308.39	59.08	26.67	14.5	10.89	73.33
1M	25	79.69	15	6.97	3.94	1.78	18.03
	100	320.59	63.08	31.41	18.82	11.47	68.59

Fig. 1. The activated carbon of two mesh sizes, 560µm and 250µm. 250µm sized charcoal particles were finer with maximum adsorption capacity to remove the impurities from the available textile wastewater in comparison to the large sized particles of activated charcoal.

Table 2. Characterization tests to check the quality parameters of the activated carbon.

Molarity of CH$_3$COOK	AC with Initial Weight (g)	pH	Iodine Number Mg/g	Moisture Content (%)	Ash Content (g)	Percentage Yield (%)
0.5M	25	8.8	317.26	2	5.42	21.84
	100	8.2	309.5	5	24.39	26.67
1 M	25	8.0	354.15	4	5.80	27.88
	100	7.9	422.8	3	22.84	31.41
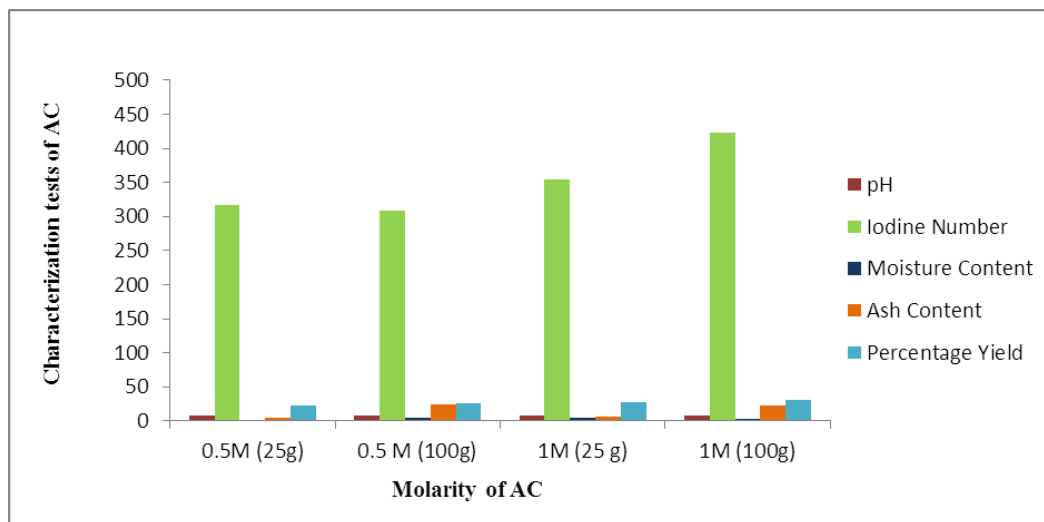
Fig. 2. Characterization tests of activated carbon of both the molarities, i.e. 0.5 M and 1M. The graphical representation of the quality tests indicates that the AC prepared was of very fine quality.

Wastewater Quality Tests

In order to check the quality of the textile industrial effluent, prior to its treatment for dye removal, pH, BOD$_5$ and COD was checked (Table 3).

Table 3. Wastewater quality indicators of the untreated and activated carbon treated textile industrial effluent.

SL	Wastewater Quality Tests	Untreated Textile Effluent	Treated Textile Effluent	NEQ Standards
1.	pH	9.4	8.2	6-9
2.	BOD$_5$ (mg/L)	38.15	36.43	80
3.	COD (mg/L)	169	161	150

Dye Removal

The percentage removal of methylene blue and reactive red 120 by AC was calculated. The results obtained indicated that the highest percentage removal was 99.71% of methylene blue. The removal of dyes amplified with increment in the sorbent dose and contact time. The AC of pore size 250µm

adsorbed the dyes more efficiently in comparison to the AC of pore size 560µm. Results indicated that with the increase in dose of the AC (sorbent), the percentage of the dyes removed from the effluent of textile industry increased. There was an increase in percentage removal of textile dyes by increasing the contact time between adsorbent and adsorbate from 0.5 to 2.5 hours. Both dyes were present in textile industrial effluent.

For Reactive Red at 536nm, there was highest dye removal percentage (38.57%) with 1M CH$_3$COOK treated AC (mesh size 250µm) in 2.5 hr contact time and sorbent dose of 0.3g/ml. Minimum percentage dye removal (2.85%) with 0.5 M CH$_3$COOK treated AC (560µm sorbent size) in 0.5 hr contact time and sorbent dose of 0.1g/ml was found (Fig. 3, 5).

For Methylene Blue spectrophotometric analysis at 668nm, there was highest dye removal percentage

(99.71%) with 1 M CH$_3$ COOK treated AC (mesh size 250µm) in 2.5 hr contact time and sorbent dose of 0.3g/ml. Minimum percentage removal (81.80%) was with 0.5 M CH$_3$COOK treated AC (560µm) in 0.5 hr contact time and sorbent dose of 0.1g/ml was obtained (Fig. 4, 6).
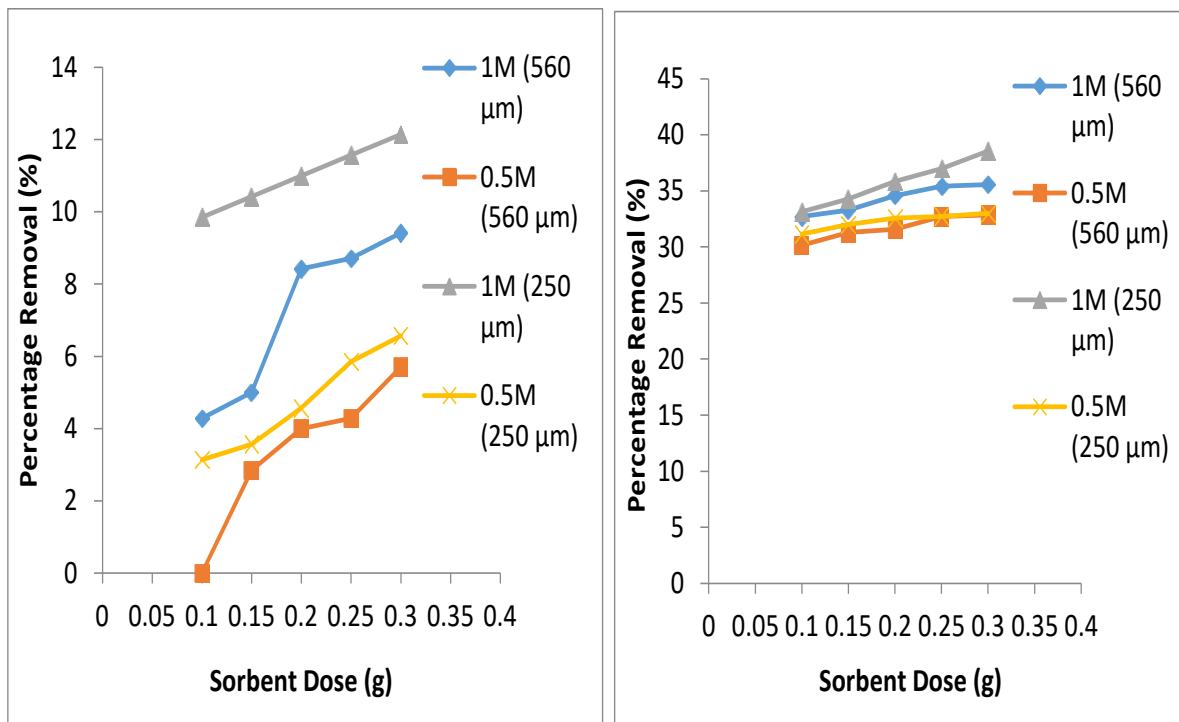
(a)   (b)

Fig. 3. The increase in percentage removal of reactive red 120 with an increase in sorbent dose of both molarities (0.5 M and 1 M) and sorbent sizes (560µm and 250µm) (a) after half an hour and (b) after 2.5 hours of the contact time.
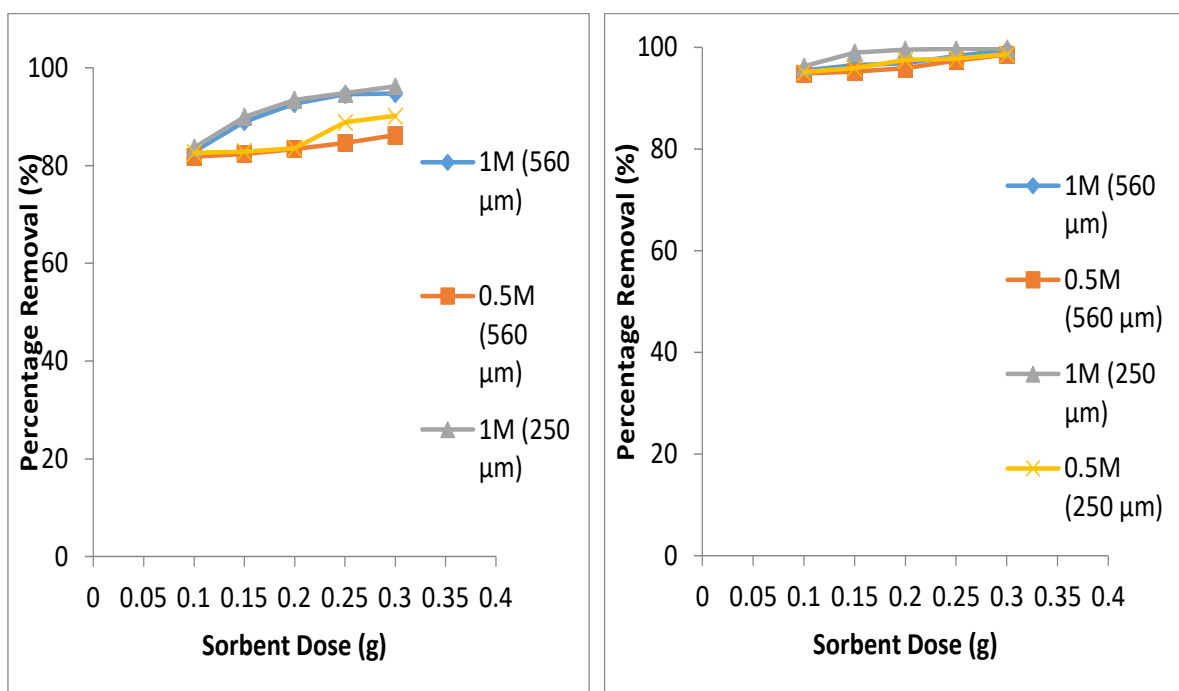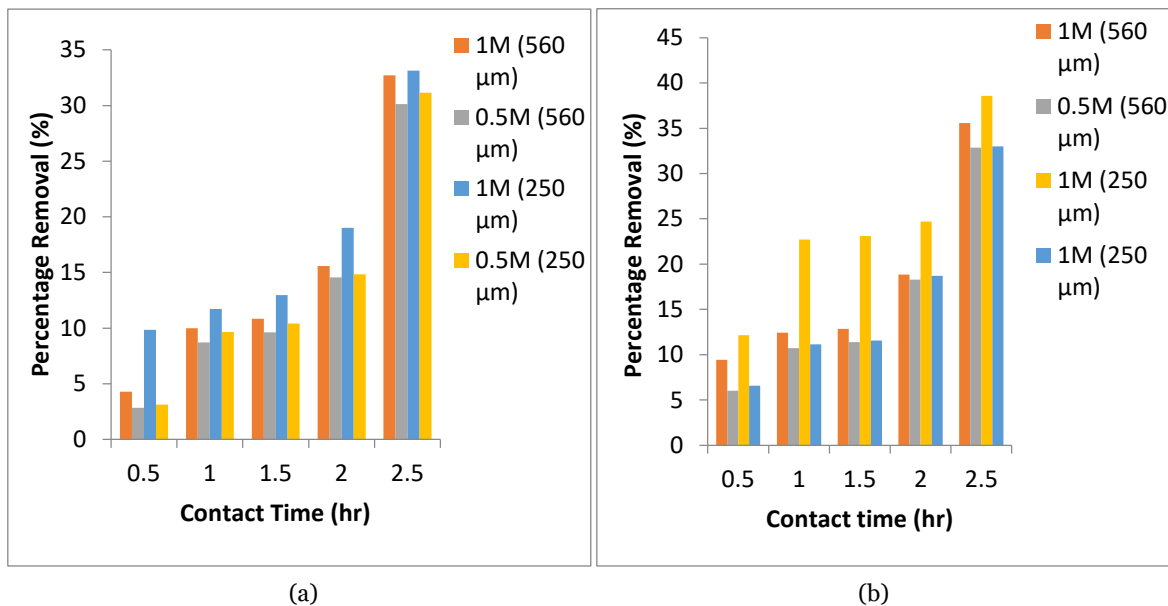

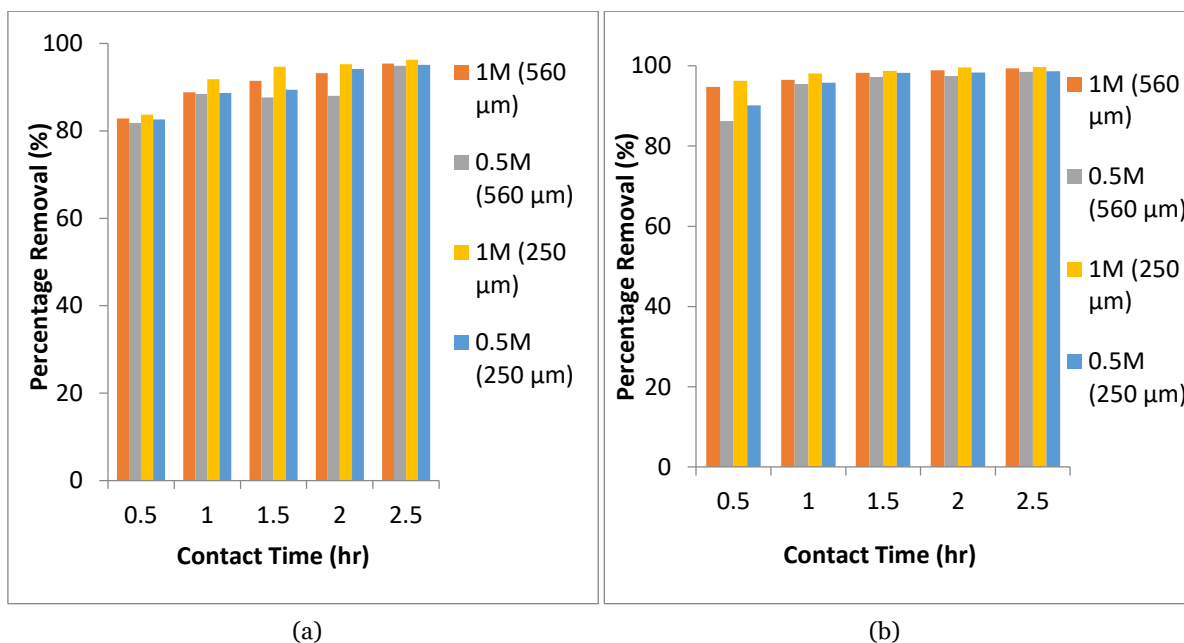(a)   (b)

Fig. 4. The increase in percentage removal of methylene blue with an increase in sorbent dose of both molarities (0.5 M and 1 M) and sorbent sizes (560μm and 250μm) (a) after half an hour and (b) after 2.5 hours of the contact time.

(a)   (b)

Fig. 5. The increase in percentage removal of reactive red 120 with an increase in contact time of both molarities (0.5 M and 1 M) and sorbent sizes (560μm and 250μm) at (a) 0.1 g sorbent dose (b) and 0.3 g sorbent dose with absorbance measured at 536nm. The highest adsorption was obtained at 2.5 hours with 0.3 g sorbent dose of 1 M (250μm) AC.

(a)   (b)

Fig. 6. The increase in percentage removal of methylene blue with an increase in contact time of both molarities (0.5 M and 1 M) and sorbent sizes (560μm and 250μm) at (a) 0.1 g sorbent dose (b) and 0.3 g sorbent dose with absorbance measured at 668nm. The highest adsorption was obtained at 2.5 hours with 0.3 g sorbent dose of 1 M (250μm and 560μm) AC.

Discussion

Activation of the spent tea leaves produces carbon activated by competent activating agent for digestion of the precursor which results in augmentation of the pores of AC (Kanawade *et al.,* 2010). Potassium acetate was used in the present research because it not only enhances the pores at micro porous level but also at meso porous level (Rao *et al.,* 2004).

The carbonization temperature influences the commotion of activated carbon by enhancing its surface chemistry. The best range for carbonization temperatures is 400-550°C (Imamoglu and Tekir, 2008). Immediately after providing the accurate temperature for carbonization, crevices or pores are formed in the crystalline structures which are responsible for the adsorption (Prahas *et al.,* 2008). The optimum temperature utilized in the current research was 500°C which resulted in the formation of AC from carbonaceous ash with very good surface characteristics as specified by results (Table 2.)

Characterization tests performed to check the quality of the AC indicated that AC in this study was of very fine value on the basis of quality parameters tested (Table 2). Iodine number helps in determination of the sorbent capacity at micro porous structural form. This test is basically concerned with the evaluation of AC on the basis of surface area having pores larger than 1nm. It was reported that, high iodine number (Mg/g) indicates large surface area and accessibility of micropores and mesopores for iodine adsorption on its surface (Hameed, 2009; Rajeshwar *et al.,* 2012). Therefore, high value of iodine number obtained in the present work indicates the presence of both micropores and mesopores on the surface of AC.

The moisture content value of the AC in the current study was within the range of 2-6%. Moreover, less value of ash content indicates the maximum adsorptive aptitude of the AC (Rajeshwar *et al.,* 2012). High ash content affects the adsorption activity of the AC because this leads to interference with the pores of the sorbent causing less adsorption. The low ash content value obtained in the present work signifies good sorbent capacity during application. The size of AC particles also has a significant effect in its efficiency for removal of dyes. More fine particles

have greater surface area and provide more pores for the adsorption process on contrary to large sized particles (Uddin *et al.,* 2009). The two mesh sizes used in the current research also elaborate the fact that high particle size AC yields less adsorption. The particle size of 250μm therefore adsorbed the dyes more effectively in comparison to 560μm.

The pH of the AC is important because it specifies the presence of net charge on the surface of the sorbent in aqueous solutions. Here, the pH was nearly alkaline, ranging from 7.9 to 8.8. The pH range which is considered best for the purification of wastewater is 6-8 (Rajeshwar *et al.,* 2012). Hence, due to the alkaline pH of the carbon, there was net negative charge on the surface of carbon which lead to the maximum percentage removal of methylene blue, being cationic in nature. The minimum adsorption of reactive red 120 which is an anionic dye, was due to the repulsion of like charges on sorbent and adsorbate surface. Reactive red 120 shows maximum adsorption to the pH of 2, with less adsorption around pH 6 and negligible adsorption is shown at a pH 12 (Auta, 2012; Majedi *et al.,* 2014). This is due to the fact that with an increase in pH, extermination of positive charged surface of AC leads to the slightest adsorption of the reactive red 120 dye due to the phenomenon of electrostatic repulsion between protonated H$^+$ ions in the dye solution and sorbent surface. Effect of pH of prepared sorbent on the adsorption of dyes is also of prime importance. Anionic dyes are adsorbed more efficiently on the AC of acidic pH due to availability of more positive charges and attraction of opposite charges. On the other hand, cationic dyes are adsorbed more effectively on the surface of AC having basic pH due to the presence of more negative charges leading to attraction phenomenon (Thirumalisamy and Subbian, 2010; Rahman *et al.,* 2012; Majedi *et al.,* 2014). In case of methylene blue dye adsorption, the maximum percentage removal owes to the fact that there is attraction between OH$^-$ ions of the surface carbon and the cationic nature of methylene blue.

The pH of the textile industrial wastewater was also checked which was found above the normal range of pH which is 6-9 according to NEQs (Tsai *et al.,* 2008;

Ahmaruzzaman and Gayatri, 2010). Any sample of water having pH above or below this range needs to be treated before its release in the nearby lakes and streams. The pH of the water sample used in the existing study was 9.4 which is not suitable for consumption and after treatment with AC pH was reduced to 8.2.

The chemical oxygen demand of textile wastewater was also checked which was above its recommended value as per NEQs is 150mg/L. In the present case the value was 169mg/L before treatment, but after filtration through AC it was reduced to 161 mg/L. This value is still higher than the standard value, most probably because COD cannot be removed after single filtration step. Several processing procedures are adopted to overcome COD issues. BOD of any wastewater tells us about the dissolved oxygen required by aerobic microorganisms to break the organic molecules over a certain time. The value of biological oxygen demand is always less than the chemical oxygen demand. In this study, the BOD_5 value was obtained within the normal range.

Adsorption process of AC has certain characteristics on which it depends. Firstly, molecules of adsorbate migrate to the surface of AC, secondly, they diffuse to the surface layer of AC through the periphery layer, and then adsorption phenomenon occurs at the surface of AC. Finally, some of the particles diffuse into the interior of the porous structure of the AC for enhanced adsorption process (Bhatti *et al.,* 2015). Therefore, contact time plays a very significant role in performing ideal adsorption process between the molecules of the dyes and the surface of AC.

The effect of sorbent dose and the contact time was studied in the present work. According to the results, with an increase in sorbent dose from 0.1g to 0.3g, a successful increment in the percentage removal of dyes was observed. This was due to the fact, that by keeping the amount of effluent constant and by increasing the sorbent dose, more sights are available for the attachment of adsorbate (dye) on the surface of AC, hence increasing the surface area of carbon for adsorption phenomenon. According to the results, the

maximum percentage removal was observed at 0.3g dose in 15ml of effluent.

Moreover, due to the consumption of nearly all sights available on the surface of AC for the adsorption of dyes at higher contact time indicates that almost the percentage removal has slight difference at various sorbent doses because at certain point all the sights are occupied and if the contact time continues to increase then this will result in equilibrium of the reaction between adsorbate and sorbent. This is due to the reason, that with an increase in contact time, this will augment the adsorption process but after certain point there will be no further increase and reaction starts to slow down (Song, 2014). The reason is the repulsion between the cationic dye, methylene blue molecules already adsorbed on the surface of AC and the newly available molecules of dye which result in hindrance of the adsorption process.

Conclusion

Currently, AC produced from spent tea by using 0.5M and 1M potassium acetate as an activating agent has high adsorption capacity, where 1M concentration was proven more effective. AC with mesh size 250µm has proved to be more effectual in removing methylene blue and reactive red 120 dyes from textile industrial effluent with an increase in the sorbent dose and contact time. In future, we can use this process on large scale to treat textile wastewaters and take a step towards eradication of the environmental pollution.

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