Effect of Evacuation Temperature on Surface and pH of Granular Charcoal and Adsorption of Dyes

[1]Y. IQBAL, [2]IHASANULLAH, [1]S. HAIDER, [1]M. A. KHAN,
[1]I. AHMAD, [3]S.A. KHAN, [4]M. SALEEM
[1]*Department of Chemistry, University of Peshawar, Pakistan*
[2]*Nuclear Institute for Food & Agriculture, Tarnab, Peshawar, Pakistan*
[3]*PCSIR Labs, Jamrud Road, Peshawar, Pakistan*
[4]*NCE in Physical Chemistry, University of Peshawar, Pakistan*

(Received 10th January, 2005, revised 12th December, 2005)

Summary: Commercial granular charcoal was evacuated at 105, 300 and 800 °C. The effect of evacuation on pH of charcoal solution was studied. The pH showed considerable increase with evacuation. The infrared (IR) spectra of the charcoal samples before and after evacuation at these temperatures was also recorded and interpreted for the presence of both acidic and basic groups, found in the charcoal matrix. Acidic group showed considerable decrease with increase in evacuation from 105 to 800 °C while no effect was found for basic group. The adsorption studies of two dyes, methyl orange (acidic) and methylene blue (basic) were conducted at all the three evacuated granular charcoal samples at 25 °C as function of stirring time, concentration and evacuation. Adsorption equilibrium was established at four hours in case of both the dyes irrespective of their nature, concentration and evacuation temperature. Evacuation showed a positive effect on the adsorption of dyes at equilibrium time, however, highest adsorption was found at 800 °C. The adsorption data was also applied to Freundlich and Langmuir isotherms.

Introduction

Development of a country is measured from the standards of industrialization [1]. The dyeing industries like textile, printing, paper and leather tanning have a vital role in achieving high standards of industrialization and of course, form a large sub-sector of economy [2-3]. The raw materials for these industries are both organic and inorganic in origin. Organic raw material like dyes have extensive uses in textile, printing and paper industries. The pollution source from these industries particularly from textile industry, wastewater comes from the dyeing and finishing processes. Major pollutants include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity and inorganic contaminates. Most pollutants, except colour can be reduced by general chemical and physical methods [4]. The coloured effluents from these industries enter the freshwater that are not only mars the natural beauty of fresh water reservoirs but also extremely toxic to aquatic life and interfere in the transmission of sunlight thus reducing the action of photosynthesis and hence effect aquatic diversity [5]. The removal of colour in industrial effluent is a growing concern requiring remedial action. In the literature reports are present on the use of agriculture residues for the removal of colour sawdust [6], hardwood [7] and banana pith [8]. Recently efforts have been made to remove colour from aqueous medium employing charcoal using various activating methods to obtain significant results both selectively and as a whole. This approach has the potential to provide best solution to the problem.

The present research work is design to activate granular charcoal by evacuation at 105, 300 and 800 °C and to study the effect of evacuation on the equilibrium time, concentration of dyes in rela-tion to the removal of methyl orange and methylene blue.

Results and Discussion

Effect of evacuation on pH

The pH values of granular charcoal before and after evacuation at 105, 300 and 800 °C are given in the Table-1 which show increase in the pH with increase in evacuation temperature. Because the surface of charcoal is sensitive to oxygen, various surface functional groups such as carboxylic, phenolic, lactone, quinone and chromene are formed on charcoal surface due to chemisorptions of oxygen. The former groups are acidic while the later i.e. chromene is basic in nature. At 105 °C only moisture was removed from the charcoal, the pH was 7.8

where as at 300 and 800 °C the pHs were 10.1 and 11.1, respectively. This seems to be due to the removal of acidic groups from the surface, as also reported by other researchers [9-10]. Increase in the pH may also be due to the increase in water-soluble basic ash content which raises the pH in the aqueous medium [11].

Table-1: Determination of pH for granular charcoal before and after evacuation at 105, 300 and 800 °C.

	pH
Unevacuated charcoal	7.30
105 °C evacuated charcoal	7.80
300 °C evacuated charcoal	10.10
800 °C evacuated charcoal	11.10

FTIR Studies

Figure 1 shows various acidic/ basic functional groups. The number and intensity of these bands indicate that a large number of acidic/ basic functional groups are present in the charcoal matrix. The bands at 1635 and 3434 cm^{-1} are due to OH bending and stretching vibration respectively of phenolic, carboxylic acid and enol groups where as the low intensity bands at 3700 and 3400 cm^{-1} are due to free and bonded OH group of phenol. The lowering of wave number from 3700 cm^{-1} to 3400 cm^{-1} of OH stretching is due to hydrogen bonding. The appea-rance of these bands is due to OH group of acidic carboxylic, phenol and enol group present in the matrix of charcoal [12]. The region from to 1000 cm^{-1} is composed of C-O stretching of alcohal, ester, lactone and acid anhydride [13]. A sharp band at 1000 -1150 cm^{-1} is characteristic of ether due to stretching of C-O group in C-O-C and can be assigned to the presence of basic chromene. A broad band at 1800 -2000 cm^{-1} is due to stretching of C=O of carbonyl group. The bands around 1600, 1580, 1500 and 1450 cm^{-1} are for aromatic ring [14]. The medium band at 1580 cm^{-1} identifies C-H stretching in aromatic compounds i.e. almost all the groups present on the charcoal surface contains aromatic ring. The bands at 677 and 796 cm^{-1} are due to aromatic C-H bending.

The effect of evacuation temperature on surface functional groups is shown in Figures 2-4. The bands at 677, 1635 and 3600 cm^{-1} has decreased with evacuation while the bands observed at 1945 cm^{-1} for carbonyl carbon, 2355, 2673 cm^{-1} for O-H stretching of carboxylic acid has completely disappeared with evacuation indicating that the surface concentration of these functional groups decreases. A close inspection of the bands at 677, 1635, 3700 and 3400 cm^{-1} show that the relative intensity of these bands has decreased sufficiently with evacuation. The band at 1000 cm^{-1} shows almost same intensity which points toward the presence of basic groups i.e. chromene.

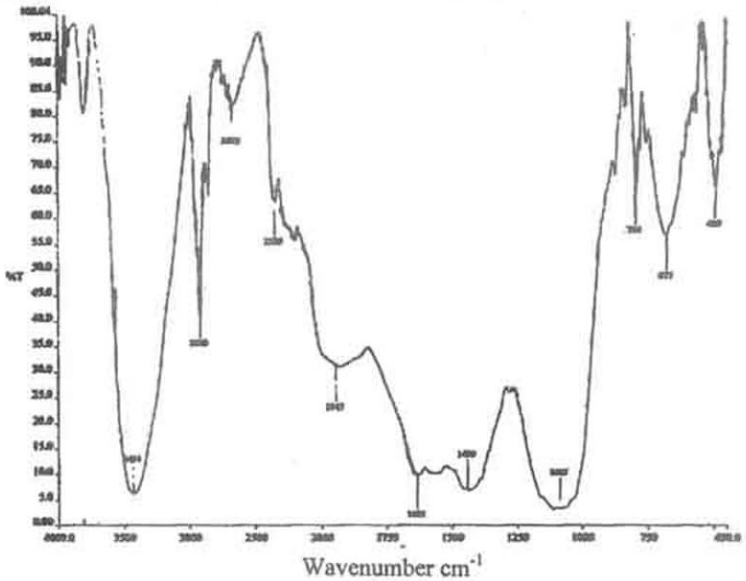

Fig. 1: IR study spectra for granular charcoal before evacuation.

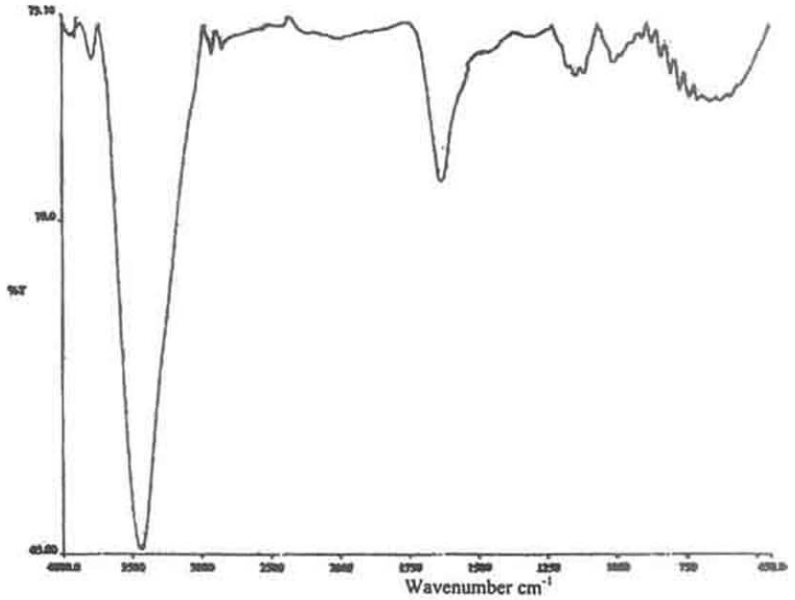

Fig. 2: IR study spectra for granular charcoal evacuated at 105°C.

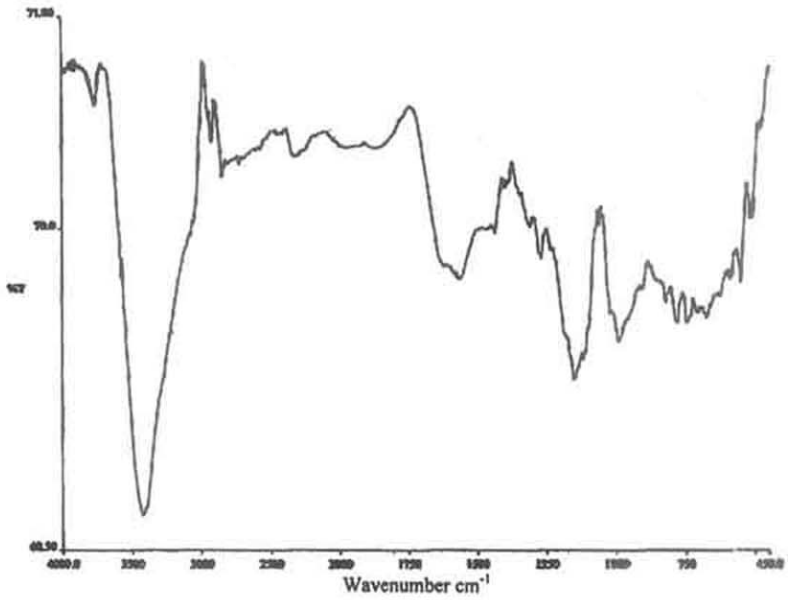

Fig. 3: IR study spectra for granular charcoal evacuated at 300 °C

Effect of time on dyes uptake

Figure 5-6 show the result of the effect of time on the uptake of two types of dyes i.e. methyl orange (acidic) and methylene blue (basic) on granular charcoal evacuated at 105, 300 and 800 °C. The uptake of both dyes increases rapidly till one hour, however after one hour of equilibration time, the dyes uptake increases slowly and becomes almost constant at four hour referred to as equilibrium time. Initially the surface to dyes interaction is more since large number of active sites is available on the granular activated charcoal but with increase in time duration the surface to dyes interaction decreases due to the

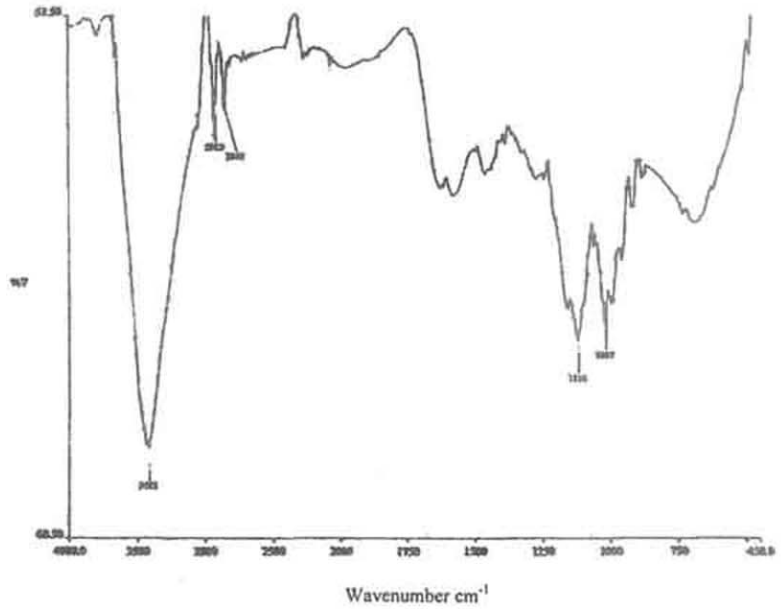

Fig. 4: IR study spectra for granular charcoal evacuated at 800°C

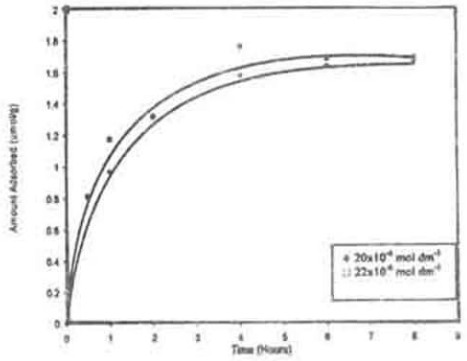

Fig. 5: Time dependence uptake study of 20 x 10^{-6} mol dm^{-3} and 22 x 10^{-6} mol dm^{-3} methyl orange on granular charcoal evacuated at 105°C.

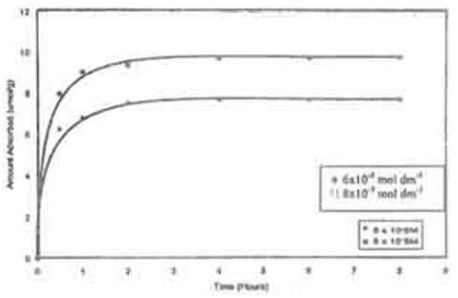

Fig. 6: Time dependence uptake study of 8 x 10^{-5} mol dm^{-3} and 8 x 10^{-5} mol dm^{-3} methylene blue on granular charcoal evacuated at 105 °C.

saturation of the surface active sites hence no further uptake occurs. The concentration of dyes show no effects on the equilibrium time i.e. the equilibrium of dyes uptake took almost same time for the increased concentration. However increased in the extent of dyes uptake can be seen from Figures 5-6. The extent of dyes uptake also increases with increase in evacuation temperature and is evident from Figures 7-8. The increasing order of the dye uptake with evacuation lies in 800 °C > 300 °C > 105 °C. The increase in the uptake of methyl orange (acidic) seems to be due to the interaction of dye molecules with basic sites on the charcoal surface, which increases with evacuation. This is evident from the increase in the pH in Table-1. However the increase in methylene blue (basic) may be, first due to the interactions of dye molecules with acidic sites, secondly due to the amphoteric nature of the basic surface functional groups.

Adsorption Study

Figures 9-10 show the adsorption of methyl orange (acidic) and methylene blue (basic) at 25 °C

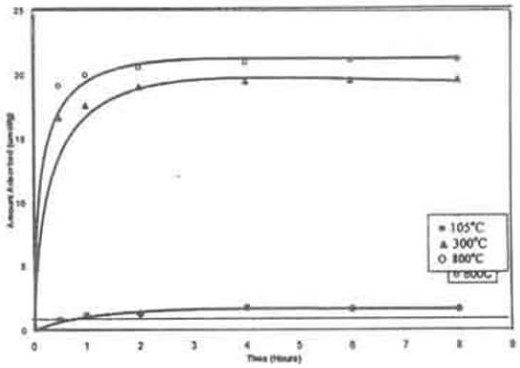

Fig. 7: Time dependence Uptake study of the methyl orange on granular charcoal evacuated at 105, 300 and 800 °C.

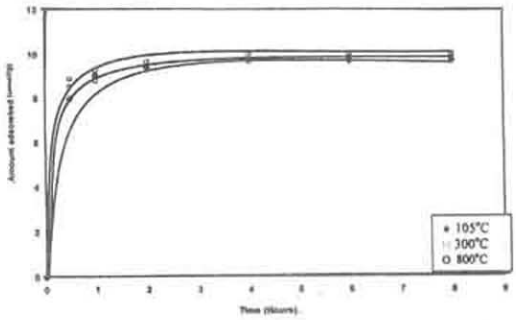

Fig. 8: Time dependence Uptake study of the methylene blue on granular charcoal evacuated at 105, 300 and 800 °C.

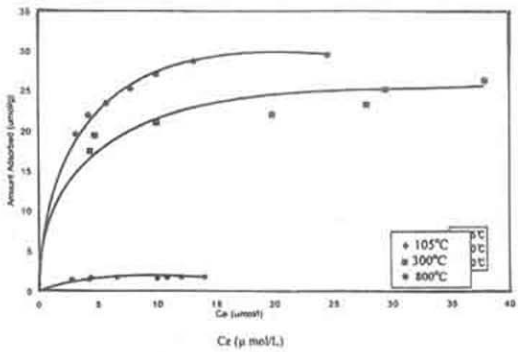

Fig. 9: Adsorption of methyl orange on granular charcoal evacuated at 105 300 and 800 °C

on granular charcoal evacuated at 105, 300 and 800 °C. Adsorption for both the dyes increase rapidly with increase in concentration, however at high

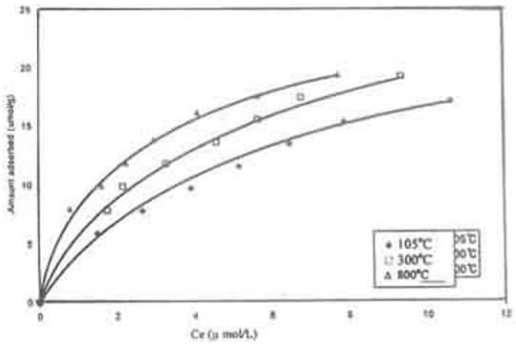

Fig. 10: Adsorption of methylene blue on granular charcoal evacuated at 105, 300 and 800 °C.

concentration of dyes, adsorption increases gradually. This show that the surface sites are non homogeneous. The easily available sites having greater pore size are of low energy and thus offer little hindrance for the molecule to occupy these sites, in contrast at high concentration the high energy binding sites with small pore size are lift for adsorption. In order to occupy these sites two types of forces hinder the adsorption process, one is the small pore size and second is the resistance offered by the adsorbed molecules for the incoming ones. Thus the surface adsorbs less number of molecules. The effect of evacuation on the adsorption behaviour of the mentioned dyes is shown in Figures 9-10, which show that adsorption increases for both the dyes with increase in evacuation temperature from 105 to 800 °C. The increase in adsorption for methyl orange is seem to be due to the increase in basic nature of the surface at 300, 800 °C. In addition to basic surface, increase in the size and number of pores/ voids with evacuation is also reported in the literature [9] where as for methylene blue (basic) the increased adsorption is due to increase in size and number of pore/voids, amphote-ric nature of basic surface functional groups and geometric dimension of the dye molecules as reported by previous authors [15].

The equilibrium date for both the dyes on granular charcoal evacuated at 105, 300 and 800 °C has been correlated with Freundlich isotherm and plotted in Figures (11-12). Freundich isotherm data obeys the linear form. The variation of Freundich plots with evacuation can be observed from the values of "k" and "n" reported in Tables-2 and 3. The values of "k" for methyl orange decreases where as "n" increases with evacuation while for methylene

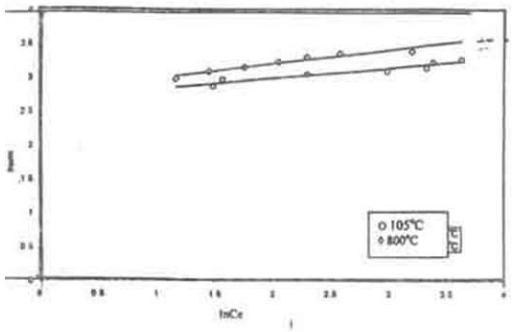

Fig. 11: Plot of Freundlich isotherm for methyl orange on granular charcoal evacuated at 300 and 800 °C.

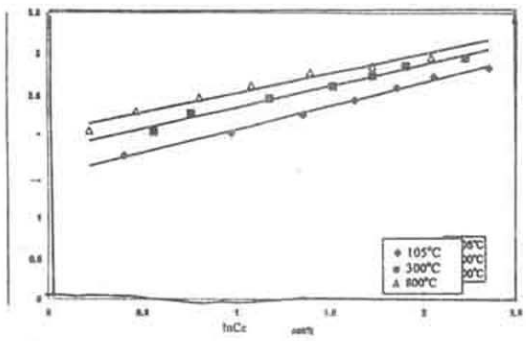

Fig. 12: Plot of Freundlich isotherm for methylene blue on granular charcoal evacuated 105, 300 and 800 °C.

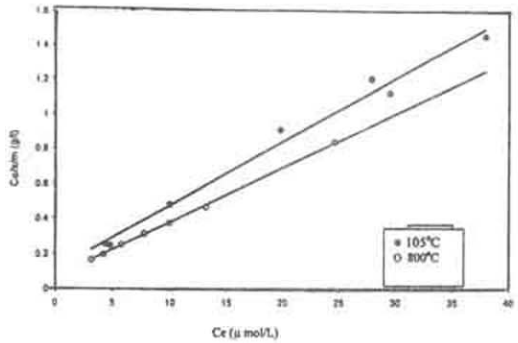

Fig. 13: Plot of Langmuir isotherm for methyl orange on Granular charcoal evacuated at 300 and 800 °C

blue the values of both "k" and "n" increases. The linear form of Langmuir is also applied to the adsorption data and plotted in Figures (13-14). Both "b" and "k" are calculated and are present in Tables-4 and 5. The variation of "b" and "k" with evacuation can be observed from the Tables-4 and 5. The "b"

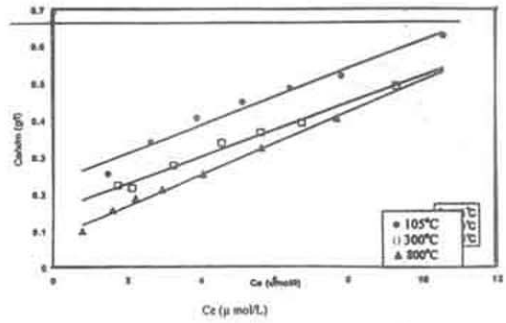

Fig. 14: Plot of Langmuir isotherm for methylene blue on granular charcoal evacuated at 105, 300 and 800 °C

values for methyl orange increases with increase in evacuation temperature. This show that the effective surface area increases to acidic dyes (methyl orange), where for methylene blue the "b" increases upto 300 °C and then decreases with further increase in evacuation. This may be due to the basicity of the surface. The "k" value increases for both the dyes with evacuation temperature.

Table-2: Freundlich constants for adsorption of methyl orange on granular charcoal evacuated at 300 and 800 °C.

Evacuation temperature	10^{-2} Slope (1/n)	10^{-6} Intercept (k)	n
300 °C	20.44	0.45	4.8
800 °C	15.08	0.29	6.6

Table-3: Freundlich constants for adsorption of methylene blue on granular charcoal evacuated at 105, 300 and 800 °C.

Evacuation temperature	10^{-2} Slope (1/n)	10^{-6} Intercept (k)	n
105 °C	56.62	0.18	1.8
300 °C	5.17	0.26	1.9
800 °C	47.12	0.32	2.1

Table 4: Langmuir constants for adsorption of methyl orange on granular charcoal evacuated at 300 and 800 °C.

Evacuation temperature	10^{-2} Slope (1/b)	10^{-3} Intercept (1/ab)	10^{6} b (μ mol/g)	K (l/g)
300°C	3.65	10.69	27.40	0.3
800 °C	3.11	0.62	32.15	0.5

Table 5: Langmuir's constants for adsorption of methylene blue on granular charcoal evacuated at 105 °C, 300 °C and 800 °C.

Evacuation temperature	10^{-2} Slope (1/b)	10^{-3} Intercept (1/ab)	10^{6} b (μ mol/g)	K (l/g)
105 °C	3.77	235.00	26.53	0.1
300°C	3.75	158.80	28.01	0.2
800 °C	4.17	85.90	23.98	0.4

Experimental

Commercial grade granular charcoal was used as adsorbent. Various chemical and thermal treatments of the sample were carried out as reported earlier [9].

Instrumentation

1. FTIR Spectrometer (Model Perkin Elmer 16pc)
2. UV Spectrophotometer (Schimadzu Model160-A)
3. Spetronic20D Spectrophotometer (Milton Roy Company, Belgium)

Determination of pH

The 10 % (w/v) mixture of charcoal and double distilled water was stirred for 3hours. The pH of the granular charcoal before and after evacuation was measured

FTIR studies

5mg of pure and evacuated granular charcoal at 105, 300 and 800 °C before adsorption was mixed with KBR crystal and grounded into fine powder. The fine powder was shaped into a disc form under hydraulic pressure of 10 torr and exposed to infrared radiation in FTIR spectrometer.

Determination of wavelength

Wavelength of maximum absorption for methyl orange and methylene blue was determined in dilute solution by UV spectrophotometer.

Adsorption studies

Adsorption equilibrium studies were carried out by stirring 0.5 g of the adsorbent and 50 cm^3 of adsorbate in conical flask, closed by stopper for different durations of time at 25 °C. All the experi-ments were performed in a thermostat by batch technique. The resultant solutions were analyzed by spectronic 20D spectrophotometer at 460 nm and 663 nm respectively.

References

1. R. Duka, P Hernandez, G. Fate and T.C. Hjuct, *Air and Soil Pollution*, **90**, 531 (1996).
2. F.K Bangesh, S.Alam and M Iqbal, *J. Chem. Soc. Pak.*, **23**(4), 215 (2001).
3. M Saeed and S.K.N. Hyder, "Economics of Pakistan" pub Imtiaz - 38 under Bazer (Lah): p 97 (2000).
4. Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen and M.N. Ahmad, *Wat. Res.*, **34**(3), 927 (2000).
5. M.N. Khan, S. Anila, Z. Uzma and Fahimuddin, *Pak. J. Anal. Chem.*, **3**(1), 2 (2002).
6. V.J.P. Poots, G. Mckay and J.J. Healy, *Wat. Res.*, **10**, 1067 (1976)
7. H.M. Asfour, O.A. Fadali, M.M. Nassar and M.S. El-Geundi, *J. Chem. Tech. Biotechnol.*, **35A**, 21 (1985)
8. C. Namasivayan, N. Kanchana and R.I. Yamuna, *Waste Manage.*, **13**, 89 (1993).
9. Y. Iqbal, S. Alam and M. Ishaq, *J. Chem. Soc. Pak.*, **22**(4), 281 (2000).
10. F. Haghseresht and G.Q. LU, *Carbon*, **37**, 639 (1999)
11. M. Arsala Khan, *Pak. J. Physical Chemistry*, **3**,: 35 (1993).
12. Y.R. Sharma, Elementary organic spectroscopy FTIR principles and application, S. Chand and Company Ltd. Ram Nagar. New Delhi (2000).
13. P.S Kalsi, Spectroscopy of organic compounds, Pub. Wiley Estern Ltd (1993).
14. J. Coats, Interpretation of infrared spectra. A practical approach, Coates Consulting, New Town, U.S.A (1990).
15. C. Shuixia and L.Z. Hammin, *Journal Lizi Jiauhuan Yuxifu*, **16**(3), 267 (2000).