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Removal of Metanil Yellow from its Aqueous Solution by Fly Ash and Activated Carbon Produced from Different Sources

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Abstract: The present study has been undertaken to observe the relative efficiency of removal of metanil yellow from its aqueous solution by using different adsorbents like fly ash and activated carbon produced from different sources i.e. coconut shell, mehagani saw dust, and rice husk. It has also been observed that the rate of adsorption is highly dependent on contact time, adsorbent dose, pH, and initial concentration of the dyestuff. Rate of removal has been observed to increase with increasing contact time and adsorbent dose but with decreasing initial concentration. Higher removal has been observed generally in acidic range. Adsorptions by the adsorbents under investigation follow the Freundlich and Langmuir isotherm models where Freundlich and Langmuir constants have also been determined at different temperatures. Isotherms have been used to obtain the thermodynamic parameters like free energy, enthalpy and entropy of adsorption. Kinetic studies showed that all the adsorbents follow first order adsorption rate model with respect to the dye solution concentration. Various kinetic parameters such as first order adsorption rate constant, mass-transfer co-efficient, pore-diffusion constant, and activation energy of adsorption were evaluated to establish the mechanism. Adsorption processes were found to be endothermic, spontaneous, and pore-diffusion controlled for all the adsorbents. Among the adsorbents used in this study, activated carbon produced from mehagani saw dust has been

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found to be the most effective, which remove almost 100% metanil yellow from its 1000 ppm aqueous solution.

Keywords: Adsorption, dyestuff, metanil yellow, activated carbon, adsorption isotherms, enthalpy, free energy, entropy, activation energy, mass-transfer co-efficient, pore diffusion

INTRODUCTION

Metanil Yellow is a major pollutant which is generally used in textile, tannery, paper, soap, cosmetics, polishes, and wax industries. It is generally applied as a dyeing and coloring agent in the above-mentioned industries. The effluents from these units contain metanil yellow among many other dyestuffs. It imparts color to water and lowers its aesthetic value. Metanil yellow is also used for coloring a wide variety of food stuffs though it ranks at the top amongst non-permitted colors. Its toxic and carcinogenic nature has also been reported in the literatures. Acute toxicity of metanil yellow to heteropneustes fossils has also been reported. Besides mortality other adverse effects of metanil yellow to the test fish included loss of body weight, changes in body colors, restlessness, and jerky and random movements (1, 2). It has also been found that even a very low concentration of metanil yellow increases the COD value of water significantly and affects the light penetration depth adversely. Presence of the said dye even in a very small amount imparts considerable color to the industrial wastewater stream and thus makes it unsuitable for recycling. It becomes therefore essential to remove the dye as far as possible prior to final disposal as the biological treatment process is unable to remove this dyestuff.

Adsorption process has been found to be very effective amongst various methods used for the removal of dyes. Activated carbon is the most commonly used adsorbent. However, due to its high cost and about 10–15% loss during regeneration, attempts have been made by several investigators to replace it by unconventional adsorbents like fly ash, bottom ash, peat, lignite, bagasse pith, wood, saw dust, rice husk, coconut shell, tea waste, wheat husk etc. The adsorption characteristics have been widely investigated by them for removal of coloring dyes, heavy metals, phenolic compounds, and refractory organics and reported in literatures (3–16).

The nature of the sites that are responsible for basic properties and the resultant reactivity of many solid carbon surfaces in solution is not fully understood. Carbon surfaces acquire a basic character on high temperature (>973 K) heat treatment (17). Moreover, it has been reported that most carbons contain a small amount of inorganic impurity which can also influence their acid-base response in solution (18). Nevertheless, the pure organic portion alone has been found to manifest their surface basicity in several ways, such as a pH value above 7, a positive external surface charge, and acidic uptake (16). Makey et al. (19) reported the removing behavior of eight dyes (two cationic and six anionic) by using six different natural adsorbents. They concluded that with the exception of one adsorbent, all adsorbents showed high capacity for cationic dyes. Juang et al. (20) also studied the effect of dye charge on adsorption onto activated carbon. Higher capacity and faster adsorption kinetics were observed for cationic dyes in their findings. According to them this preference is due to electrostatic attraction between electron donor groups (i.e. negative surface charge) on the carbon surface and the positive charges on the dyes. In fact it has been reported that activated carbon adsorbents, generally, carried a net negative surface charge in solution and it is believed to be of significance for the adsorption process (21).

Apart from these, adsorption of dyes from solution onto activated carbon is controlled by many factors. Some of these factors depend on adsorbent characteristics such as the magnitude of the surface area and porosity and others are related to the chemical content of the carbon surface and the interaction of the adsorbate to the adsorbent surface. Various results have been reported in the literatures in this direction relating activated carbon capacities and performance for various types of dyes. Furthermore, a number of proposed mechanisms regarding the above were also reported (20, 22–25). These mechanisms are based, mainly, on the electrostatic attraction between the dye charge and adsorbent surface charge during the adsorption process. According to Low et. al. (24) most biological adsorbents like maize, cob, bagasse pith, and peat wood, are more efficient in attracting cationic than anionic dyes which is due mainly to coulombic attraction between the negative surface charge of the adsorbents and the positively charged dyes.

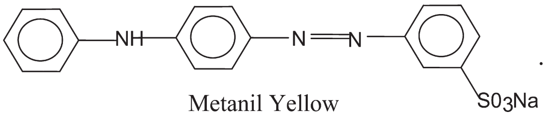
Dyestuffs have been essential materials for human society and at the same time they are the major constituent of all organic pollutants. So removal of dyes from the industrial waste water is a matter of great concern at the present time. Several conventional methods are utilized for the separation of dyestuffs, but all of these procedures have a number of limitations. Adsorption technique is now-a-days widely used and various types of adsorbents are employed for the removal of dyes. Among the adsorbents, activated carbons are the most effective for the separation of dyestuffs from aqueous solutions, but its high cost acts as a deterrent for its extensive use. Considering the above aspects, in the present investigation attempts have been made to observe the relative efficacy of low cost adsorbents like fly ash and activated carbons produced from waste material such as saw dust, coconut shell and rice husk for the removal of metanil yellow from its aqueous solution.

In order to have a better understanding of the mechanism of the effect of surface chemistry and adsorbent characteristics on the selectivity of the adsorbents produced from different sources towards the dye under investigation, attempts have also been made in the present study to explain the results in terms of the surface or total acidity/basicity in case of fly ash and surface acidity/basicity area of the adsorbents.

EXPERIMENTAL

Adsorbate Specifications

Metanil Yellow, monoazo C.I. acid yellow 36 (13065), FW: 375, is manufactured by Loba Cheme, India and supplied in powdered form. The dye is miscible with water producing an orange to yellow solution depending on concentration and pH. The molecular structure of metanil yellow is given below



Metanil Yellow

The λ_{max} of the dye is 440 nm; pH and COD of 1000 ppm solution have been found to be 9.50 and 1274 mg/litre respectively.

Adsorbents Specifications

The adsorbents used in this study are fly ash (FA) and granular activated carbon prepared from coconut shell (CAC), mehagani saw dust (SDC), and rice husk (RHC). Mehagani saw dust collected from a saw mill was sieved to obtain the desired size fractions and then washed with deionized water for several times to remove the sand followed by filtration under vacuum. The completely dried saw dust was carbonized in a closed atmosphere in a centrally electrically heated horizontal semi-rotatable fine control (100%) furnace with superheated steam feeding arrangement. The temperature was slowly raised to 450°C and this temperature was maintained for one hour. Then the carbonized saw dust was activated by injecting superheated steam (pressure 1–1.5 kg/cm^2) into the furnace for one hour. During the activation period the temperature of the furnace was maintained at 750°C. The activated

Table 1. Parameters for the preparation of activated carbons

	Carbonization		Steam activation		
Adsorbent	Temp. (K)	Duration (hr)	Activation temp. (K)	Duration (hr)	Steam pressure (kg/cm^2)
Coconut shell	773	1	1098	2	1–1.5
Rice husk	623	1	873	1	1.5
Mehagani saw dust	723	1	1023	1	1–1.5

Table 2. Chemical composition of fly ash

Combustible	Fe_2O_3	SiO_2	P_2O_5	TiO_2	CaO	MgO	Others
10%	1.32%	76%	0.54%	1.00%	6.23%	4.3%	0.5%

carbon so produced was kept in the furnace overnight for cooling. The prepared activated saw dust carbon was collected from the furnace and kept in a desicator for experimental use. Similar procedure was followed for the preparation of activated carbon from rice husk except the temperatures for carbonization and activation which were 350°C and 600°C respectively. Coconut shells were crushed to tiny particles with the help of a crusher and then the above-mentioned method was adopted to get activated carbon from it. For coconut shell the carbonization and activation temperatures and activation period were 500°C, 825°C, and two hours respectively. Parameters for the preparation of activated carbons from saw dust, coconut shell and rice husk are presented in Table 1. Fly ash has been obtained from Bandel thermal power plant, West Bengal, India. Chemical composition of fly ash is given in Table 2. Table 3 contains some important characteristic values of the adsorbents used in the present study.

EXPERIMENTAL PROCEDURE

Batch experiment has been carried out by shaking the adsorbent in powdered form with 50 ml of metanil yellow solution taken in a well-stoppered bottle in a constant temperature shaking bath of constant speed (400 rpm). The effects of different parameters e.g., contact time, adsorbent dose, pH, and initial concentration of the dye, on adsorption of metanil yellow has been studied. The effect of each parameter on adsorption has been studied keeping all other

Table 3. Characteristics of adsorbents

Adsorbents	SDC	RHC	CAC	FA
Bulk density (Kg/m^3)	251.53	317.21	703.76	810.56
Solid density (Kg/m^3)	1400	1290	1250	1060
Moisture content (%)	0.54	6.52	13.92	0.2066
Ash content (%)	6.45	43.97	3.44	98.31
Particle size (mesh)	200–150	200–150	200–150	200–150
Surface area (m^2/g)	516.1	263.5	500.0	6.7
Porosity (%)	0.338	0.165	0.325	0.09

SDC = Saw dust carbon; RHC = Rice husk carbon; CAC = Coconut shell activated carbon; FA = Fly ash.

parameter values at a constant level. Concentrations of dye in solution were measured using a UV-Visible spectrophotometer (Model No.GS5701A, Electronic Corporation of India Limited) in the visible range in the absorbance mode. Absorbance values were recorded at the wavelength of maximum absorbance of metanil yellow ($\lambda_{max} = 440$ nm). Absorbance was found to vary linearly with concentration and dilutions were made when the absorbance exceeded 0.9. The powdered adsorbent was separated from the treated dye solution by filtering the slurry with whatman filter paper No. 42. The first portion of the filtrate was discarded to eliminate the effects of any adsorption onto filter paper. The concentration of metanil yellow in the treated solution was also measured by centrifuging the slurry at 2200 rpm speed for 15 minutes and it was found to be almost identical with the concentration obtained by previous method. So paper filtration has negligible influence on the amount of adsorbed dye during solid-liquid separation. Consequently, all the concentration measurements were made after filtration by whatman filter paper No. 42.

In order to study the adsorption equilibrium, varying amount of adsorbents was shaken with 50 ml of 1000 ppm dye solution at constant speed (400 rpm) and temperature for five hours. The contact time was fixed up on the basis of batch experiments. The equilibrium adsorption studies were conducted for three different temperatures i.e.; 20, 30, and 40°C. The equilibrium concentrations have been determined by converting absorbencies (for absorbencies above 1.600, the solutions were diluted in constant ratio) to concentrations using the standard linear calibration curve.

Surface/Total Acidity and Basicity of the Adsorbents

Both the acidity and basicity of adsorbents have been determined using titration methods (17). The measured acidity and basicity are surface acidity and surface basicity in cases of carbon adsorbents whereas in case of fly ash those are total acidity and total basicity. The activated carbon adsorbents were washed several times with distilled water and then dried at 100°C for 24 hours prior to titration. All chemical reagents used in the titration were of analytical grade and supplied by E. Merck (India) Ltd.

Surface/Total Acidity

5.0 g of adsorbent was put into contact with 50 ml of 0.01 N Standard NaOH solution within a stoppered glass bottle and the mixture has been shaken in an automatic shaker for 5 hours at 30°C and then the mixture has been filtered with whatman filter paper No. 42 and back titrated with 0.01 N standard HCl solution. The surface/total acidity of the adsorbents has been determined and expressed in mequi/g of adsorbents.

Table 4. Surface acidity, basicity and pH of solutions of activated carbon adsorbents

Absorbents	Surface acidity (mequi/g)	Surface basicity (mequi/g)	pH, 10% solution (w/v)
RHC	0.08806	0.3464	8.59
CAC	0.00243	0.9404	10.19
SDC	0.01257	2.3263	10.23

Surface/Total Basicity

The surface/total basicity of an adsorbent has been quantified by mixing 0.5 g of adsorbent with 50 ml of 0.1 N standard solution of HCl. The mixture has been shaken in an automatic shaker for 3.5 hours at 30°C. An aliquot of the supernatant has been filtered and back titrated with 0.1 N standard NaOH solution.

pH of Adsorbent Solution

The pH values of adsorbent solutions have been measured after 2.5 hours stirring of 10% (W/V) mixture of adsorbent and distilled water.

Table 4 shows the surface acidity, surface basicity of activated carbon adsorbents and pH values of their solutions. The total acidity, total basicity of fly ash, and the pH of its 10% (W/V) solution are 0.04702 mequi/g, 0.0494 mequi/g and 6.83 respectively.

RESULTS AND DISCUSSION

The surface basicity of SDC is much greater than that of CAC, RHC and total basicity of FA, as shown in Table 4. The values are 2.3263, 0.9404, 0.3464, and 0.0494 mequi/g respectively. As shown in Table 3. the surface area of SDC is higher than that of CAC, RHC and FA. The values are 516.1, 500.0, 263.5, and 6.7 m^2/g respectively. So in order of surface/total basicity, SDC $\gg$ CAC $>$ RHC $>$ FA and in order of surface area, SDC $>$ CAC $>$ RHC $\ggg$ FA, however the order of surface/total acidity is RHC $>$ FA $>$ SDC $\gg$ CAC. In the present investigation it has been found that the difference in adsorption capacity of metanil yellow by SDC, CAC, RHC, and FA is, mainly, influenced by surface/total basicity as well as to some extent by the surface area. In order to have a better understanding of the mechanism of adsorption, in the present study the influences of contact time, adsorbent dose, initial concentration of the dye, and pH of the dye solution on adsorption have also been studied for determining the relative capacity of the adsorbents. It has been found that the results follow the same trend with the values of the surface/total basicity and surface area of the adsorbent. Percentage removal of dye from the solution and the amount of the dye in the adsorbent phase was calculated as follows:

$$\%\text{Removal} = \left[\frac{(C_0 - C_t)}{C_0}\right] \times 100 \tag{1}$$

$$q_t = [(C_0 - C_t)v]/w \tag{2}$$

$$q_e = [(C_0 - C_e)v]/w \tag{3}$$

Where C_0, C_e, and C_t are concentrations of dye solution at initial and equilibrium conditions and after adsorption at time t (min) respectively, v is the volume of the metanil yellow solution (L) and w is the weight (g) of the adsorbent; q_t and q_e are the amount of dye in adsorbent phase at time t and at equilibrium respectively.

Effect of Contact Time

Effect of contact time on percentage removal is illustrated in Fig. 1. The experiment has been conducted with following conditions. 50 ml of 1000 ppm metanil yellow solution, pH: 6.45, was stirred with one gram of adsorbent in an automatic shaker with constant speed (400 rpm) and the temperature was maintained at 30°C. It has been found that the removal by SDC and FA come to a saturation after about half an hour whereas removal by CAC and

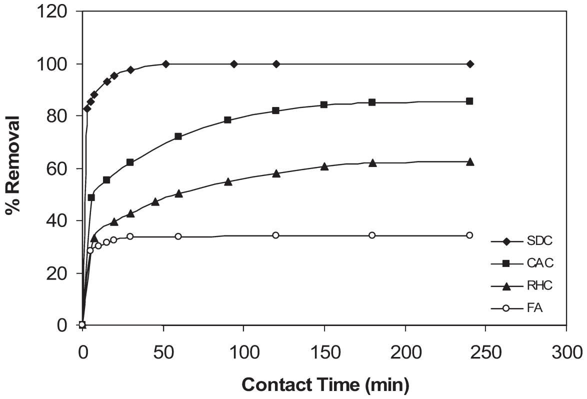


Figure 1. Effect of contact time on removal of metanil yellow. (Conditions: Concentration of dye solution: 1000 ppm; pH: 6.45, adsorbent dose: 1.0 g, volume of dye solution: 50 ml, temperature: 30°C.)

RHC take three hours to reach saturation. Therefore, the equilibrium time was set conservatively at five hours for further experiments. After three hours of stirring the percentage removal values of metanil yellow from its aqueous solution by SDC, CAC, RHC, and FA have been compared and found to be 99.9, 85, 62, and 34 respectively. The comparative removal capacity of the adsorbents with respect to contact time is in conformity with the order of surface/total basicity and surface area of the adsorbents under investigation.

It may be mentioned that though the surface areas of SDC and CAC are close to each other, 516.1 m^2/g and 500.0 m^2/g respectively, the adsorption capacity of SDC is greater than that of CAC. This is due to the greater surface basicity of SDC in comparison to that of CAC. Therefore it may be concluded that the adsorption of metanil yellow from its solution onto activated carbon is mainly controlled by the surface chemistry of the activated carbon and therefore dependent on the interaction of the dye to the activated carbon surface rather than the magnitude of the surface area.

Again, the surface area of RHC is much greater than that of FA, viz.263.5 m^2/g and 6.7 m^2/g respectively, but this is not reflected accordingly in their adsorption capacities. The observed adsorption capacities of RHC and FA are mainly dependent on surface/total basicity rather than the surface area. However, the relative adsorption capacities of CAC and RHC with respect to contact time as shown in Fig. 1 are observed to be influenced by their surface basicity as well as surface area.

The poor adsorption capacity of FA compared to activated carbons may be explained on the basis of the fact that the surface of fly ash contains mainly oxygen atoms and hydroxyl groups. It has been reported that these hydroxyl groups mainly control the acid base character and reactivity of the surface (16). On the other hand, the activated carbon surfaces contain different types of surface groups such as carboxylic, phenolic, carbonyl, and etheric etc. This diversity of surface groups probably makes the acid-base character much more versatile (26) and therefore the reactivity of the surface much higher than fly ash.

Effect of Adsorbent Dose

Effect of adsorbent dose on percentage removal of metanil yellow has been shown in Fig. 2. The experiment has been performed by stirring 50 ml of 1000 ppm metanil yellow solution pH: 6.45 with varying dose of adsorbents for 30 minutes in an automatic shaker with constant speed (400 rpm) and the experimental temperature was maintained at 30°C. It has been observed that almost 100 percent removal of metanil yellow has been attained after 30 minutes of stirring by one gram of SDC and by 3 grams of CAC though the adsorbents have an almost similar surface area. So this difference in the adsorption capacity is related to their surface basicity.

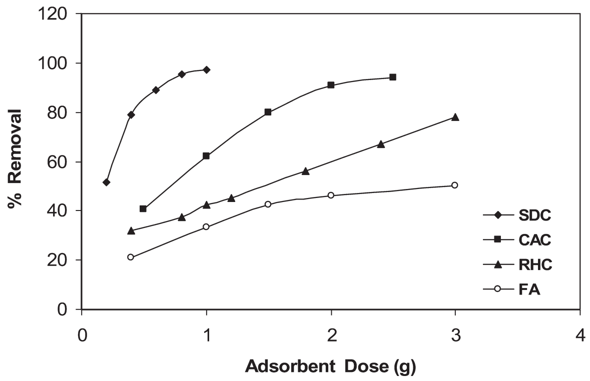


Figure 2. Effect of adsorbent dose on removal of metanil yellow. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH: 6.45, volume of dye solution, temperature: 30°C, contact time: 30 min.)

Three grams of each CAC and RHC remove almost 100 percent and 78 percent metanil yellow respectively after 30 minutes of stirring. These adsorption capacities are in good agreement with the order of the surface area and surface basicity of CAC and RHC.

Three grams each of RHC and FA remove 78 and 50 percent metanil yellow respectively after 30 minutes of stirring, though the surface area of RHC is much greater than that of FA. It is therefore evident that the surface/total basicity of the adsorbents have played a significant role on the relative adsorption capacities of RHC and FA.

In general, the percentage removal of metanil yellow increases with increasing dose of the adsorbents. However, after certain optimum dose no appreciable increase in percentage removal has been observed as the attainments of equilibrium become slower. The overall effect of the adsorbent dose on removal of metanil yellow follows mainly the order of surface/total basicity and to some extent the order of surface area of the adsorbents under investigation.

Effect of Initial Concentration

The effect of initial concentration on percentage removal of metanil yellow is illustrated in Fig. 3. The experiment has been conducted by stirring one gram of adsorbent with 50 ml of metanil yellow solution, pH: 6.45, at different concentration for 30 minutes in an automatic shaker with constant speed (400 rpm) and the temperature was maintained at 30°C.

The percentage removal has been found to increase with decrease in initial concentration of the adsorbate. However, within the range of concentration used in this investigation, the percentage removal by SDC has been

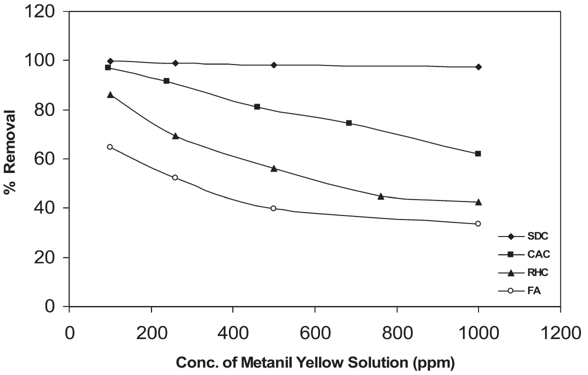


Figure 3. Effect of concentration on removal of metanil yellow. (Conditions: Volume of the dye solution-50 ml, pH: 6.45, contact time-30 min, adsorbent dose-1.0 g, temperature 30°C.)

found to remain almost unaffected and the values are almost 100%. This may be due to great extent of affinity of the adsorbent particle for the dye molecule under investigation. The removal–concentration relations in the cases of CAC, RHC, and FA are exponential in nature. Similar observations have also been reported in other literatures (5, 6, 8, and 14).

It has been observed that almost 100 percent removal of metanil yellow occurred at concentrations of 1000 ppm, 400 ppm, 200 ppm, and 10 ppm by one gram each of SDC, CAC, RHC, and FA respectively. This order of initial concentration for removing the dye from its aqueous solution is in agreement with the order of surface/total basicity of the adsorbents. The values of surface/total basicity of SDC, CAC RHC and FA are 2.3263, 0.9404. 0.3464, and 0.0494 respectively. It has also been observed that the surface areas of CAC (500.0) and RHC (263.5) also play a significant role in controlling the relative adsorption capacities with respect to initial concentration of the metanil yellow.

Effect of pH

The effect of pH on percentage removal is shown in Fig. 4. The experiment has been performed by stirring one gram of adsorbent with 50 ml of 1000 ppm metanil yellow solution with varying pH for 30 minutes in an automatic shaker with constant speed (400 rpm) and the temperature was maintained at 30°C. As shown in Fig. 4 the adsorption capacities of SDC, CAC, RHC, and FA decrease with increasing pH. Lower pH has been found to be favorable for the removal of metanil yellow, an acid dye, by using CAC, RHC, and FA. This is in agreement with the result obtained by Gupta et al. (8) using an acid dye omega chrome M.E. Owing to high surface basicity the activated carbon adsorbents, SDC, CAC, and RHC, carry a net negative

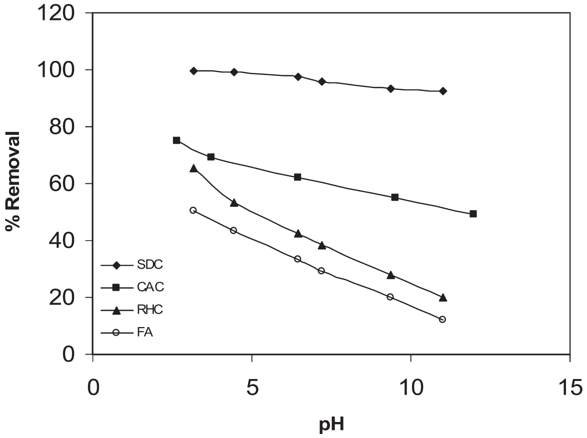


Figure 4. Effect of pH on removal of metanil yellow. (Conditions: Conc. of metanil yellow solution: 1000 ppm, contact time: 30 min, adsorbent dose: 1.0 g, volume of solution: 50 ml, temperature; 30°C).

surface charge in solution, which is manifested by the pH values of their 10% solution above 7.00. So the adsorption of metanil yellow, an acid dye, is favored at lower pH range by SDC, CAC, and RHC, because in acidic solution the negative surface charge of the activated carbon adsorbent is neutralized and thereby diminishes the repulsion between the carbon surface and dye anion. Again the favorable separation of metanil yellow by fly ash in acidic pH can be explained on the basis of an ion-exchange mechanism. The metal oxides present in fly ash form an aquo-complex with water and develop a positively charged surface at lower pH and so attract the negatively charged dye ion by strong electrostatic attraction.

Adsorption Isotherms

The adsorption isotherms were determined for various adsorbent-dye systems. The removal of metanil yellow with four adsorbents i.e., SDC, CAC, RHC, and FA has been studied at 20, 30, and 40°C to determine the adsorption isotherms and various thermodynamic parameters. The extent of adsorption of metanil yellow is found to increase with temperature (Tables 5 and 6), indicating the process to be endothermic in nature. The increase in the removal of the dye with temperature may be owing to the enhanced rate of intraparticle diffusion of the adsorbate because the diffusion is an endothermic process. The increment in the adsorption behaviors suggests that the active surface centers available for adsorption have increased with temperature. This may also be a result of an increase of the mobility of the large dye molecule with the rise of temperature. An increasing number of molecules may also

Table 5. Freundlich constants for adsorption of metanil yellow on various adsorbents

Temp. (°C)	a_F	n	r^2
SDC			
20	11.61	3.03	0.9876
30	25.44	4.18	0.9873
40	35.39	4.59	0.9278
CAC			
20	3.23	2.20	0.9867
30	5.33	2.38	0.9877
40	16.41	3.67	0.9869
RHC			
20	0.60	1.69	0.9960
30	1.60	2.04	0.9912
40	4.25	2.53	0.9843
FA			
20	0.37	2.21	0.9961
30	0.54	2.39	0.9953
40	0.73	2.46	0.9934

a_F: Freundlich constant [$\mathrm{mg \cdot g^{-1}(L \cdot mg^{-1})^{1/n}}$], n: Freundlich constant (dimensionless), r^2: correlation coefficient.

Table 6. Langmuir constants and separation factor for adsorption of metanil yellow on various adsorbent

Temp. (°C)	Q_0 ($\mathrm{mg \cdot g^{-1}}$)	$b \times 10^3$ ($\mathrm{L \cdot mg^{-1}}$)	R_L	r^2
SDC				
20	111.67	8.15	0.1093	0.9997
30	118.25	21.49	0.0445	0.9873
40	132.19	40.96	0.0238	0.9992
CAC				
20	79.69	4.27	0.1898	0.9982
30	90.28	6.83	0.1277	0.9986
40	99.15	14.90	0.0629	0.9969
RHC				
20	52.83	1.68	0.3731	0.9978
30	54.87	3.17	0.2398	0.9968
40	65.96	6.25	0.1379	0.9979
FA				
20	11.12	2.59	0.2786	0.9989
30	11.90	3.38	0.2283	0.9995
40	12.87	4.64	0.1773	0.9943

Q_0, b: Langmuir constant, R_L: separation factor, r^2: correlation coefficient.

acquire adequate energy to perform an interaction with active sites of the adsorbent surface. Moreover, increase of the temperature may produce a swelling effect within the internal structure of the adsorbents, enabling the large dye molecules to penetrate further, as reported by Gupta et al. (27) for adsorption of basic dye on activated carbon and activated slag.

Freundlich Isotherms

The Freundlich equation may be written as follows:

$$q_e = a_F C_e \frac{1}{n} \qquad \text{(Nonlinear Form)} \tag{4}$$

$$\log q_e = \log a_F + \frac{1}{n} \log C_e \qquad \text{(Linear Form)} \tag{5}$$

Where C_e is the liquid phase equilibrium concentration of the adsorbate ($\mathrm{mg \cdot L^{-1}}$) and q_e is the solid phase equilibrium concentration of the adsorbate ($\mathrm{mg \cdot g^{-1}}$) i.e., the amount of metanil yellow adsorbed per unit weight of adsorbent. The Freundlich constant a_F ($\mathrm{L \cdot g^{-1}}$) denotes the energy of adsorption which varies as a function of surface coverage (q_e) which in turn related with the surface area of the adsorbent. The other Freundlich constant n (dimensionless) is the heterogeneity factor which has a higher value for more heterogeneous surfaces (28). The plots of log q_e versus log C_e for different adsorbents at 30°C are illustrated in Fig. 5. It shows a linear relationship, which confirms the applicability of Freundlich model. The

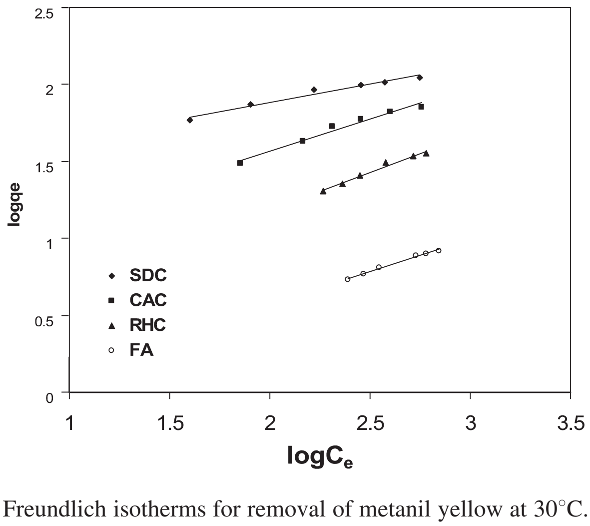


Figure 5. Freundlich isotherms for removal of metanil yellow at 30°C. (Conditions: Concentration of metanil yellow solution: 1000 ppm, pH: 6.45, contact time: 5 hours.)

Freundlich constants a_F and n are calculated from plots and their values at three different temperatures, i.e., 20, 30, and 40°C for different adsorbents are listed in Table 5. It is observed from the table that the values of a_F are much higher for saw dust carbon (SDC) at all of the three temperatures under investigation. The a_F values indicate that the energy of metanil yellow adsorption of the adsorbents are of the order SDC > CAC > RHC > FA. So the energy of adsorption of the acid dye is directly related to the surface area of the adsorbents. From the values of n it is evident that the surfaces of SDC and CAC are more heterogeneous than that of RHC and FA. For each of the four adsorbents $1/n$ value is less than unity and this indicates that adsorption of metanil yellow is favorable for the adsorbents under investigation. Furthermore, the value of a_F and n increases with increasing temperature for all of the four adsorbents indicating better adsorption at higher temperature.

Langmuir Isotherms

The Langmuir equation may be written as follows:

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \quad \text{(Nonlinear Form)} \tag{6}$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad \text{(Linear Form)} \tag{7}$$

Where C_e is the liquid phase equilibrium concentration of the adsorbate ($\mathrm{mg \cdot L^{-1}}$) and q_e is the solid phase equilibrium concentration of the adsorbate ($\mathrm{mg \cdot g^{-1}}$) i.e., the amount of metanil yellow adsorbed per unit weight of adsorbent; Q_0 and b are the Langmuir constants, Q_0 signifies monolayer adsorption capacity at a particular temperature ($\mathrm{mg \cdot g^{-1}}$) and b is related to the energy of adsorption ($\mathrm{L \cdot mg^{-1}}$) ($b \alpha\, \mathrm{e}^{-\Delta G/RT}$) and it is the reciprocal value of the concentration at which half the saturation of the adsorbent is attained.

The plots of C_e/q_e versus C_e for the adsorption of metanil yellow by different adsorbents at 30°C are illustrated in Fig. 6 and it shows a linear relationship which confirms the applicability of the Langmuir model for the adsorption processes under investigation. The Langmuir constants of different adsorbents for the adsorption of metanil yellow at 20, 30, and 40°C are calculated from the plots and are given in Table 6. The adsorption capacities of all of the four adsorbents increase with increasing temperature which indicates that adsorption of metanil yellow is favorable at a higher temperature for all the adsorbents under investigation and the adsorption processes are endothermic in nature. The values of Langmuir constant Q_0 indicate that metanil yellow adsorption capacities of SDC, CAC, RHC, and FA are of the order: SDC > CAC > RHC > FA, which is directly related with the surface area and surface/total basicity of the said adsorbents. The values of the Langmuir constant, b, which is related to the energy of adsorption, show favorable adsorption of metanil yellow

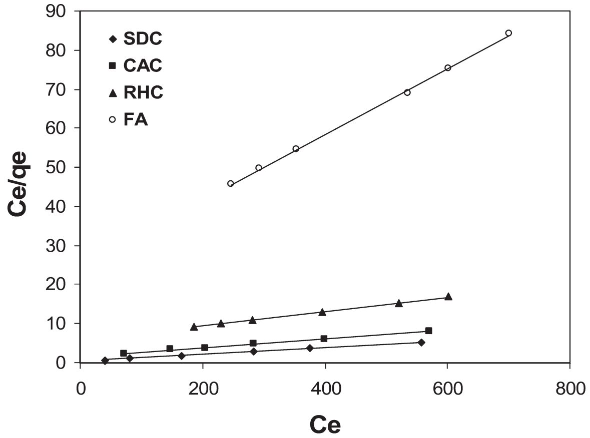


Figure 6. Langmuir isotherms for removal of metanil yellow at 30°C. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH: 6.45, contact time: 5 hours.)

by SDC and CAC. The Langmuir constant b is a characteristic of an adsorbent and also related to its surface area. The feasibilities of the adsorption processes are calculated by the dimensionless constant called separation factor (29), R_L.

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

Where b is the Langmuir constant and C_0 is the initial concentration. The calculated values of the separation factor R_L are included in Table 6. The magnitude of the R_L values, i.e., $0 < R_L < 1$, indicates the favorable adsorption of metanil yellow by the adsorbents under investigation.

Thermodynamic Parameters

Thermodynamic parameters like enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) for metanil yellow separation by different adsorbents were calculated by using the following equations:

$$\ln b = \ln b' - \frac{\Delta H}{T} \tag{9}$$

$$\Delta G = -RT \ln b \tag{10}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{11}$$

Where b is the Langmuir constant which have different values at 20, 30, and 40°C. The enthalpy changes (ΔH) were determined graphically by plotting ln b against 1/T, which gives straight lines for different adsorbent-dye systems

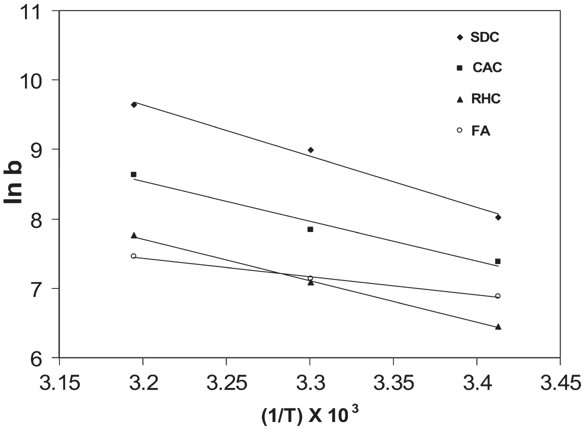


Figure 7. Variation of ln (*b*) with reciprocal of temperature for the separation of metanil yellow by different adsorbents.

(Fig. 7). The values of ΔG and ΔS were computed numerically and presented in Table 7. The positive values of enthalpy change confirm the endothermic nature of metanil yellow adsorption by all the adsorbents, i.e., SDC, CAC, RHC, and FA.

Furthermore, negative values of free energy change indicate feasibility and spontaneous nature of adsorption and high affinity of the adsorbents for metanil yellow. ΔG values decreases with an increase of the temperature, which indicates that better separation is obtained at a higher temperature. The positive values of the entropy change indicate the increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the adsorbents toward metanil yellow.

KINETIC STUDIES

On the basis of the effect of adsorbent dose, the amount of different adsorbents has been kept 20 g/L in all the kinetic experiments. Preliminary investigations

Table 7. Thermodynamic parameters for metanil yellow separation by different adsorbents

	$-\Delta G$ (KJ/mol)				
Adsorbents	20°C	30°C	40°C	ΔH (KJ/mol)	ΔS (J/k · mol)
SDC	19.55	22.66	25.09	61.68	278.8
CAC	17.97	19.77	22.45	47.54	223.4
RHC	15.70	17.84	20.19	50.11	224.5
FA	16.76	18.00	19.42	22.21	132.9

ΔG: free change, ΔH: enthalpy change, ΔS: entropy change.

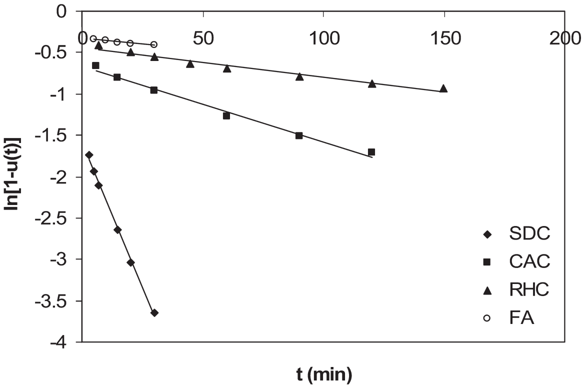


Figure 8. First order sorption kinetics of metanil yellow onto various adsorbents at 30°C. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH: 6.45, adsorbent dose: 1.0 g.)

on the rate of uptake of metanil yellow by different adsorbents indicated that the processes were quite rapid and typically 50–80% of the ultimate adsorption occurred within half an hour of contact time.

The adsorption of dyes can be considered as a reversible reaction with equilibrium established between two phases. It has been observed that the adsorptions of metanil yellow by the four adsorbents, i.e. SDC, CAC, RHC, and FA follow the first order rate equation as proposed by Bhattacharya and Venkobachar (30):

$$\ln[1 - \mu(t)] = kt \tag{12}$$

Where $\mu\ (t)$ represents fractional attainment of equilibrium at time t and k is the rate constant of the process. The straight line plots of ln $[1 - \mu\ (t)]$ against t were obtained for the adsorbents under investigation which are shown in Fig. 8.

The values of k at 30°C are included in Table 8, which reveal that the rate constant of SDC is much higher than the other three adsorbents and FA has the

Table 8. Activation energy and first order rate constant of metanil yellow adsorption by different adsorbents

Adsorbent	Rate constant (k) (min^{-1})	Activation energy (E) (KJ/mol)
SDC	7.00×10^{-2}	13.00
CAC	9.13×10^{-3}	29.07
RHC	3.56×10^{-3}	39.12
FA	2.95×10^{-3}	45.99

lowest rate constant. The rate constant values are in conformity with other adsorption batch experiments performed with the dye and four adsorbents.

Kinetic data were analyzed for determining the pore diffusion constant because adsorbate molecules are often diffused into the interior of a porous adsorbent in an adsorption experiment. The rate process of such pore diffusion usually depends on t^x where $x \leq 0.5$ instead of t itself. In the present investigation it was found that plots of C_t/C_0 against $t^{0.5}$ are linear. This observation is in good agreement with that of an earlier investigation (31). The rate constant of pore diffusion (k') was determined according to the following equation:

$$\frac{c_t}{c_0} = k' t^{0.5} \tag{13}$$

The variation of the fraction of metanil yellow adsorbed by different adsorbents with square root of time (sec) at 30°C is shown in Fig. 9. Values of pore diffusion constants for different adsorbent-dye systems at temperature 20, 30, and 40°C are included in Table 9.

The pore diffusion constants were very often utilized by earlier investigators (32, 33) for the determination of activation energy of separation processes at solid-solution interface. Transfer of dye molecule from an aqueous solution to a solid adsorbent surface or pores can be accepted as an activated adsorption phenomenon. The extent of activation energy of the process is determined by the Arrhenius equation:

$$\ln k' = \ln A - \frac{E}{RT} \tag{14}$$

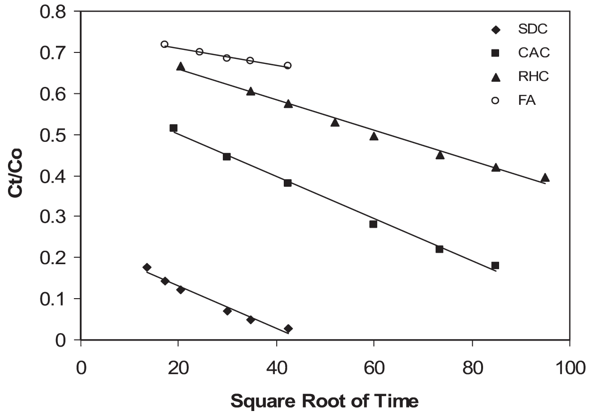


Figure 9. Variation of fraction of metanil yellow adsorbed by different adsorbents with square root of time at 30°C. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH; 6.45, adsorbent dose: 1.0 g.)

Table 9. Pore diffusion constant and mass-transfer co-efficient for metanil yellow separation by various adsorbents

Temp. (°C)	Pore diffusion constant $k' \times 10^3$ ($s^{-1/2}$)	r^2	Mass-transfer co-efficient $\beta_L \times 10^6$ ($cm \cdot s^{-1}$)	r^2
SSDC				
20	4.378	0.9971	108.98	0.9988
30	5.166	0.9880	230.40	0.9929
40	6.159	0.9861	340.86	0.9995
CAC				
20	3.380	0.9967	9.97	0.9968
30	5.131	0.9968	20.81	0.9943
40	7.244	0.9983	53.93	0.9916
RHC				
20	2.086	0.9970	6.56	0.9985
30	3.709	0.9946	11.91	0.9882
40	5.815	0.9961	21.46	0.9974
FA				
20	1.132	0.9917	5.50	0.9977
30	2.100	0.9900	8.18	0.9771
40	3.785	0.9882	14.93	0.9944

r^2: Correlation coefficient.

Plotting ln k' against $1/T$ gives straight lines (Fig. 10) for different adsorbents, from which the activation energy of the adsorption processes were determined and presented in Table 8.

The mass-transfer co-efficient for the separation processes of metanil yellow from aqueous solution by the adsorbents under investigation were

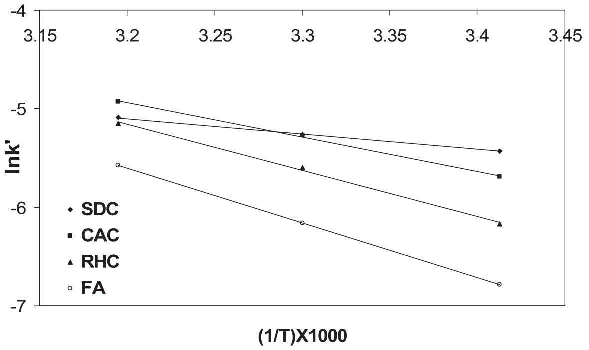


Figure 10. Variation of pore diffusion constants of metanil yellow with reciprocal of temperature for different adsorbents. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH: 6.45, adsorbent dose: 1.0 g.)

determined according to the Mckay et. al. model (34) with the help of the following equation:

$$\ln\left(\frac{c_t}{c_0} - \frac{1}{1+mk}\right) = \ln\left(\frac{mk}{1+mk}\right) - \left(\frac{1+mk}{mk}\right)\beta_L S_S t \tag{15}$$

Where C_t, C_0, m, β_L, S_S, and k are the concentration of the adsorbate at time t (min), initial concentration of the adsorbate, mass of the adsorbent per unit volume of particle free slurry (g/L), mass-transfer co-efficient, outer surface of the adsorbent per unit volume of particle free slurry (cm^{-1}), and a constant obtained by multiplying Langmuir constants Q_0 and b respectively. Plotting the left-hand side of Equation (15) against t gives straight lines for various temperatures for each adsorbent. Figure 11 shows such linear plots for different sadsorbents at 20°C. The values of m and S_S were calculated from the following relations:

$$m = \frac{w}{v} \tag{16}$$

$$S_S = \frac{6m}{d_p \rho_p (1 - \xi_p)} \tag{17}$$

Where w, v, d_p, ρ_p, and ξ_p are the weight of the adsorbent (g), volume of the particle free slurry (L), particle diameter of the adsorbent (cm), density of the adsorbent particle (g/L), and porosity of the adsorbent particle. The values of the mass-transfer co-efficient were determined from the slope of the curves and presented in Table 9. The values of β_L show that the velocity of the adsorbate transport from the solution phase to the solid phase is quite rapid for SDC, CAC, and RHC. Fly ash has the lowest β_L value indicating its least suitability for metanil yellow separation among the four adsorbents

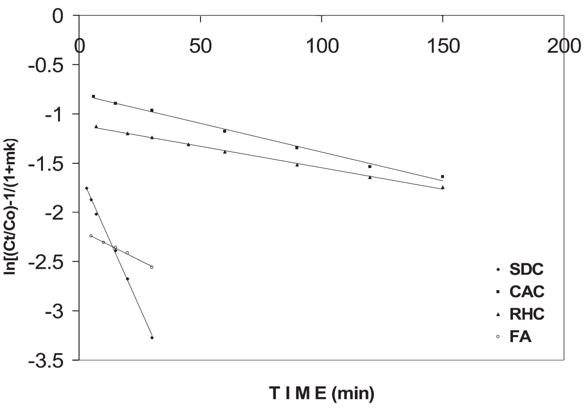


Figure 11. Variation of ln [(C_t/C_0) – 1/(1 + mk)] with time for mass transfer of Metanil yellow at 20°C. (Conditions: Conc. of metanil yellow solution: 1000 ppm, pH: 6.45, adsorbent dose: 1.0 g.)

Table 10. Adsorption capacities of dyes on various adsorbents

Name of the dye	Low cost adsorbents	Adsorption capacity (mol/g)
Malachite green	Activated carbon developed from fertilizer waste	12.50×10^{-5} (27)
Crystal violet	Wollastonite	2.17×10^{-6} (35)
Crystal violet	Fly ash	9.76×10^{-5} (36)
Malachite green	Blast furnace slag	10.52×10^{-5} (27)
Methylene blue	Activated carbon derived from coconut shell fibers	5.24×10^{-5} (37)
Methylene blue	Perlite	8.21×10^{-5} (38)
Alizarin yellow	Bottom ash	8.30×10^{-5} (39)
Metanil yellow	Activated carbon prepared from saw dust	3.53×10^{-4} (Present Study)

which is also supported by other kinetic and thermodynamic parameters evaluated in the present investigation.

CONCLUSION

The results of the present investigation show that activated carbon prepared from mehagani saw dust, coconut shell, and rice husk have greater adsorption capacity than fly ash with regard to the removal of metanil yellow from its aqueous solution. Among four adsorbents used in this investigation the activated carbon prepared from mehagani saw dust showed the maximum adsorption capacity of metanil yellow from its aqueous solution. The adsorption is highly dependent on contact time, adsorbent dose, initial concentration, and the pH of the dye solution and the adsorptions obey both Freundlich and Langmuir models. Mainly the surface/total basicity and to some extent the surface area of the adsorbents have been found to have a significant role in adsorbing the dye under investigation from its solution. Adsorption processes are spontaneous, and endothermic in nature and controlled by pore diffusion and surface adsorption and they follow the first order rate mechanism. The rate constant of the saw dust carbon - metanil yellow system was found to be much greater than that of the other three adsorbent-dye systems. Prepared activated carbons showed greater affinity for metanil yellow and among the four adsorbents the activated carbon prepared from saw dust has the highest affinity for the dye under investigation. The sorption capacity of the saw dust activated carbon is much greater than that of other available low cost adsorbents used by the earlier investigators (Table 10). The present study revealed that the activated carbon developed from saw dust could be successfully employed as a good adsorbent for dye removal.

NOMENCLATURE

t	time (min)
C_t	concentration of metanil yellow solution at time t ($mg \cdot L^{-1}$)
C_0	initial concentration of metanil yellow solution ($mg \cdot L^{-1}$)
C_e	equilibrium concentration of metanil yellow in solution ($mg \cdot L^{-1}$)
v	volume of metanil yellow solution (L)
w	weight of adsorbent (g)
r^2	correlation co-efficient
SE	standard error
m	mass of the adsorbent particle per unit volume of particle-free slurry (gL^{-1})
β_L	mass-transfer co-efficient ($cm \cdot s^{-1}$)
S_S	outer surface of adsorbent particles per unit volume of particle free slurry (cm^{-1})
d_p	adsorbent particle diameter (cm)
ρ_p	density of adsorbent particle ($g \cdot L^{-1}$)
ξ	porosity of adsorbent particle (%)
k'	pore diffusion constant ($s^{-1/2}$)
q_t	concentration of metanil yellow in adsorbent at time t ($mg \cdot g^{-1}$)
q_e	equilibrium concentration of metanil yellow in adsorbent ($mg \cdot g^{-1}$)
a_F	Freundlich constant, measure of adsorption capacity [$mg \cdot g^{-1} (L \cdot mg^{-1})^{1/n}$]
n	Freundlich constant, measure of intensity of adsorption (dimensionless)
Q_0	Langmuir constant, signifies monolayer adsorption capacity at a particular temperature ($mg \cdot g^{-1}$)
b	Langmuir constant related to energy of adsorption ($L \cdot mg^{-1}$)
R_L	sseparation factor (dimensionless)
T	solution temperature (K)
k	First order rate constant of adsorption (min^{-1})
E	activation energy ($KJ \cdot mol^{-1}$)
ΔH	enthalpy change for adsorption of metanil yellow ($KJ \cdot mol^{-1}$)
ΔG	free energy change for adsorption of metanil yellow ($KJ \cdot mol^{-1}$)
ΔS	entropy change for adsorption of metanil yellow ($J \cdot mol^{-1}$)

REFERENCES

1. Mall, I.D. and Kishore, K.M. (1995) Treatment of metanil yellow Bearing Wastewater using Coal Flyash. Proceedings of the 11th National Convention of Chemical Engineers, India, Sept. 28–29.
2. Goel, K.A. and Gupta, K. (1995) Acute toxicity of metanil yellow to heteropneustes fossilis. *Indian J. Environ. Health.*, 27: 266.

3. Asfour, H.M., Nassar, M.M., Fadli, O.A., and El-Geundi, M.S. (1985) Colour removal from textile effluent using hardwood and saw dust as an adsorbent. *J. Chem. Technol. Biotechnology.*, 35A: 28.
4. Mckay, G., Ramprasad, G., and Pratap Mowli, P. (1986) Equilibrium Studies for the adsorption of dyestuffs from aqueous solutions by low cost materials. *Water, Air and Soil Pollution*, 29: 273.
5. Khare, S.K., Pandey, K.K., Srivasteva, R.M., and Singh, V.N. (1987) Removal of victoria Blue from aqueous solution by Fly Ash. *Chem. Tech. Biotechnology*, 38: 99.
6. Kumar, S., Upadhyay, S.N., and Upadhyay, Y.D. (1987) Removal of phenols by adsorption on fly ash. *J. Chem. Tech. Biotechnology*, 37: 2.
7. Allen, S.J., Mckay, G., and Khader, K.Y.H. (1989) Equilibrium adsorption isotherms for basic dyes onto lignite. *J. Chem. Tech. Biotechnology*, 45: 291.
8. Gupta, G.S., Prassad, G., and Sing, V.N. (1990) Removal of chrome dye from aqueous solutions by mixed adsorbents: flyash and coal. *Water Research*, 24: 45.
9. Lens, P.N., Vochten, P.M., Spellers, L., and Verstruete, W.H. (1994) Direct treatment of domestic wastewater by percolation over peat, bark and wood chips. *Water Research*, 28 (1): 17.
10. Dutta, S., Basu, J.K., and Ghar, R.N. (2001) Studies on adsorption of p-nitrophenol on charred saw-dust. *Sep. Puri. Technology*, 21: 227.
11. Al-Degs, Y., Khraishesh, M.A.M., Allen, S.J., and Ahmad, M.N.A. (2001) Sorption behavior of cationic and anionic dyes from aqueous solution on different types of activated carbons. *Sep. Sci. Technology*, 36 (1): 91.
12. Lee, C.K., Low, K.S., and Gan, P.Y. (1999) Removal of some organic dyes by acid–treated spent bleaching earth. *Environ. Technology*, 20: 99.
13. Mall, I.D. (1993) Studies on treatment of pulp and paper mill effluent: removal of dyes by adsorption. Ph.D Dissertation, Banaras Hindu University.
14. Mall, I.D., Mishra, N., and Mishra, I.M. (1994) Removal of organic matters from sugar mill effluent using bagasse, fly ash, activated carbon. *Research and Industry*, 39: 115.
15. Mall, I.D. and Upadhyay, S.N. (1995) Removal of basic dyes from waste water using boiler bottom ash. *Indian J. Environ. Health*, 37 (1): 1.
16. Al Degs, Y., Khraisheh, M.A.M., Allen, S.J., and Ahmad, M.N. (2000) Effect of carbon Surface chemistry on the removal of Reactive Dyes from textile effluent. *Water Research*, 34 (3): 927.
17. Puri, B.R. (1970) *Chemistry and Physics of Carbon*; Marcel Dekker: New York.
18. Parks, G.A. (1965) The isoelectric point of solid oxide, solid hydroxides and aqueous hydroxo complex systems. *Chem. Revs.*, 65: 177.
19. Mckay, G., Ramprasad, G., and Mowli, P. (1987) Desorption and regeneration of dye colors from low cost materials. *Water Research*, 21 (3): 375.
20. Juang, R.S. and Swei, S.L. (1996) Effect of dye nature on its adsorption from aqueous solution onto activated carbon. *Sep. Sci. Technology*, 31: 2143.
21. Weber, W.J. (1965) Sorption from solution by porous carbon. Principles Appl: Water Chem. Proc. Rudolfs Res. Conf. 4th Rutgess, State University, New York; 89.
22. El-Geundi, M. (1991) Colour removal from textile effluents by adsorption techniques. *Water Research*, 25 (3): 271.
23. Sethuraman, V. and Raymahashay, C. (1975) Colour removal by clays, kinetic study of adsorption of cationic and anionic dyes. *Environ. Sci. Technology*, 9: 13.
24. Low, K.S. and Lee, C.K. (1997) Quternized rice husk as sorbents for reactive dyes. *Bioresour. Technology*, 61: 121.

25. Lee, C.K., Low, K.S., and Chung, L.C. (1997) Removal of some organic dyes by hexane–extracted spent bleaching earth. *J. Chem. Tech. Biotechnology*, 69: 93.
26. Leon, Y., Leon, C.A., and Radovic, L.R. (1994) *Chemistry and Physics of Carbon*; Marcel Dekker.
27. Gupta, V.K., Srivastava, S.K., and Mohan, D. (1997) Equilibrium uptake, sorption dynamics, process optimizatation and column operation for removal recovery of malachite green from wastewater using activated carbon and activated slag. *Ind. Eng. Chem. Research*, 36 (6): 2207.
28. Walker, G.M. and Weatherley, L.R. (2001) Adsorption of dyes from aqueous solution—the effect of adsorbent pore size distribution and dye aggregation. *Chem. Eng. Journal*, 83: 201.
29. Jain, A.K., Gupta, V.K., Bhatnagar, A., and Suhas (2003) Utilisation of industrial waste products as adsorbents for the removal of dyes. *J. Hazardous Material*, B101: 31.
30. Bhattacharya, A.K. and Venkobachar, C. (1984) *J. Environ. Engg. Division. ASCE Proc.*, 110: 110.
31. Dasmahapatra, G.P., Pal, T.K., and Bhattacharya, B. (1996) Evaluation of thermodynamic parameters for separation of hexavalent chromium by fly ash. *Sep. Sci. Technology*, 31 (20): 2843.
32. Sing, A.N., Sing, D.P., and Sing, V.N. (1991) Fly ash for the treatment of Zn (II) rich effluent. *Environmentalist*, 11 (3): 217.
33. Weber, W.J. and Morris, C.J. (1963) Kinetics of adsorption of carbon from solution. *J. Sanit. Eng. Div., Am. Soc. Civ. Eng.*, 89 (SA2): 31.
34. Mckay, G., Allen, J.S., McConvey, I.F., and Otterburn, M. (1981) Transport processes in the sorption of colored ions by peat particles. *J. Colloid Interface Science*, 80 (2): 323.
35. Khare, S.K., Srivastava, R.M., Panday, K.K., and Singh, V.N. (1988) Removal of basic dye (crystal violet) from water using wollastonite as adsorbent. *Environ. Technol. Letters*, 9: 1163.
36. Mohan, D., Singh, K.P., Singh, G., and Kumar, K. (2002) Removal of dyes from wastewater using fly ash–a low cost adsorbent. *Ind. Eng. Chem. Research*, 41: 3688.
37. Singh, K.P., Mohan, D., Sinha, S., Tondon, G.S., and Gosh, D. (2003) Color removal from wastewater using low-cost activated carbon derived from agricultural waste material. *Ind. Eng. Chem. Research*, 42.
38. Dogan, M., Mahir, A., and Onganar, Y. (2000) Adsorption of methylene blue from aqueous solution onto perlite. *Water, Air, Soil Pollution*, 120: 229.
39. Gupta, V.K., Ali, I., Saini, V.K., Gerven, T.V., Bruggen, B.V., and Vandecasteele, C. (2005) Removal of dyes from wastewater using bottom ash. *Ind. Eng Chem. Research*, 44: 3655.