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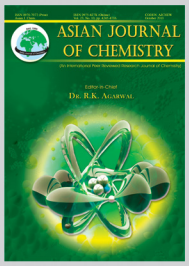

Use of Pirina Pretreated with Hydrochloric Acid for the Adsorption of Methyl Violet from Aqueous Solution

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In this study, pirina was used as an adsorbent for the removal of methyl violet from aqueous solution by adsorption technique. The pirina was pretreated with hydrochloric acid before adsorption experiments. Effects of initial dye concentration, temperature and pH on adsorption were investigated as a function of contact time. While the amount of the dye removed by pirina was increasing with increasing contact time, initial dye concentration, solution pH, it decreased with increasing solution temperature. The maximum dye removal were between 82.14 and 97.42 % under all the experimental conditions studied such as concentration, pH and temperature. Furthermore, activated carbon was also used for the adsorption of methyl violet. The maximum experimental amount of dye adsorbed obtained by using activated carbon was 189.30 mg/g per unit adsorbent. Adsorption kinetic and thermodynamic studies were also performed.

Key Words: Pirina, Activated carbon, Methyl violet, Dye, Removal, Adsorption, Kinetics, Isotherm, Thermodynamic.

INTRODUCTION

Dyes are widely utilized for various industries such as textile, dying, food, cosmetic. Many of these dyes are toxic and even carcinogenic to human health. Therefore, many researchers have been focused on the removal of coloured wastewaters from these industries. For this purpose, investigators have used physico-chemical methods such as flocculation-coagulants, ozonization, ultra-filtration, ion exchange, adsorption techniques for treating dye containing waste water[1-3]. The advantages and disadvantages of each technique are present. Of these methods, adsorption technique has been found to be an efficient and economic process for the removal of dyes and pigments as well as other organic and inorganic pollution. However, the usage of activated carbon in adsorption technique is not preferred due to its high cost. Therefore, many researchers have also extensively focused on the usage of low-cost materials such as flay ash[4], peat[5], perlite[2,6], sawdust[7], fungi[8] as adsorbent to remove undesired organic, inorganic and dye pollution by using adsorption technique, recently.

In this work, pirina, an alternative low-cost material is used as an adsorbent for the adsorption of methyl violet from aqueous solution. On the other hand, pirina is also named instead of olive stone in Turkish and Greece[9]. Pirina is a solid waste from olive oil factories. Indeed, pirina is named as remaining portion after the removal of olive oil from olive in olive oil factories and it consists of mixture of olive cake and stone[10]. It includes olive oil[10] by ratio per cent 5-6. Pirina is commonly used as a fuel as well as fertilizer and filler in the agriculture[10]. Studies with regard to the adsorption of dyes onto pirina are restricted in literature. For example, in a work done by Ugurlu *et al.*[9], olive stone (namely, pirina) activated with $ZnCl_2$ has been used as an adsorbent for the adsorption of remazol red B, an anionic dye, from aqueous solution. Aziz *et al.*[11] have studied the removal of cadmium and safranin dye using treated olive stone with sulfuric acid.

Cimino *et al.*[12] have studied the removal of cadmium by using olive cake carbon prepared by heat treatment at 700 ºC. Kula *et al.*[13] have also studied the cadmium removal from aqueous solutions by using olive stones, impregnated with $ZnCl_2$ and carbonized at 650 ºC under nitrogen atmosphere. On the other hand, Galiatsatou *et al.*[14] have also used carbonized olive stones at 850 ºC for zinc adsorption.

In this work, pirina was used as an adsorbent for the removal of methyl violet from aqueous solution by adsorption technique. The effects of contact time, initial dye concentration, solution pH and temperature and particle size on adsorption were investigated. Furthermore the isotherm, kinetic and thermodynamic studies of the adsorption process were also performed.

EXPERIMENTAL

Adsorbent: The pirina wastes used as adsorbent were provided from a private olive oil factory in Kilis, a province located in the Southern of Turkey. Activated carbon was provided from Carlo Erbaa firm and it was used without any treatment.

Preparation of adsorbent for adsorption experiments: Pirina was pretreated before adsorption experiments. Pretreated process is as follows, respectively: (i) Pirina samples were firstly crushed with a hammer and then grounded by a mill. (ii) The powdered pirina was sieved through a molecular sieve of 100-mesh. (iii) The sieved samples were treated with 0.1N HCl to remove dirt and other contaminants and then it was washed with pure water. (iv) Finally, the samples were dried in an oven at 90 ºC for 6 h to remove moisture before use and then the dried pirina was used for adsorption experiments.

Adsorbate: Methyl violet, a positively charge dye, contains a secondary amino group. The colour of this dye changes from green to blue in the pH range 2 and 3. Methyl violet has a molecular mass of 393.96 g/mol. The molecular structure of this dye is demonstrated in Fig. 1.

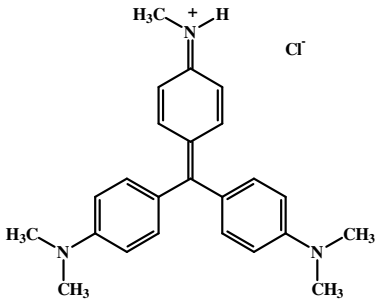

Fig. 1. Molecular structure of methyl violet

Preparation of dye solutions: The stock solutions of 1000 mg/L of methyl violet were prepared with distilled water and then they were diluted to the desired concentrations. The pH of the solutions was adjusted with 0.1N NaOH and HCl solutions using a pH meter (Elmetron pH meter).

Adsorption experiments: Adsorption experiments were carried out by mixturing 2 g of pirina with 500 mL aqueous solution of methyl violet in 1 L-Erlenmayer flasks on a temperature-controlled magnetic stirrer at different concentrations, pHs and temperatures as a function of time. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and centrifuged for 5 min at 5000 rpm. After centrifuged, supernatants was withdrawn by a very thin point micropipette, which prevents the transition to solution of pirina particles and then the supernatant samples were analyzed for the determination of the final concentration of methyl violet by using an UV-VIS spectrophotometer. The amounts of methyl violet adsorbed by pirina, q_e were calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where, q_e is the amount of dye adsorbed (mg/g). C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/g), respectively. V is the volume of the dye solution (L) and W is the weight of the adsorbent (g). The removal percentage of dye from aqueous solution can be calculated as follows:

$$\text{Removal percentage} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

Parameters on adsorption

Effect of particle size of adsorption: The effect of particle size of pirina on adsorption was selected as 45, 60, 80 and 100 mesh for the initial methyl violet solution of 40 mg/L at 20 ºC, pH 9 and 400 rpm, respectively.

Effect of concentration on adsorption: The initial concentrations of methyl violet on adsorption were selected as 20, 40, 60, 80 and 100 mg/L at 20 ºC, pH 9 and 400 rpm.

Effect of pH on adsorption: The initial pHs of methyl violet solutions on adsorption were adjusted as 3, 5, 7 and 9 for the initial concentration of 40 mg/L at 20 ºC and 400 rpm, respectively. The pHs of dye solutions were adjusted using 0.1N HCl and NaOH solutions by using a pH meter.

Effect of temperature on adsorption: The temperatures of methyl violet solutions on adsorption were selected as 20, 30, 40 and 50 ºC for the initial concentration of 40 mg/L at pH 9 and 400 rpm, respectively.

RESULTS AND DISCUSSION

Effect of contact time on adsorption: The effect of contact time on the amount of methyl violet adsorbed by pirina was investigated under all the experiment conditions such as initial dye concentration, pH, temperature and particle size. A rapid adsorption occurs within first 5 min and thereafter the gradual increase in adsorption maintains for 90 min under all conditions studied. For the concentrations of 20, 40, 60, 80 and 100 mg/L, after 90 min, with the further increment in the time, the amount of dye adsorbed does not change and even from time to time, very small decreases in the amount of the dye adsorbed are observed, indicating desorption. Therefore, the time of 90 min is accepted as the optimum contact time (equilibrium time) under all conditions studied. Similar results have been reported for the adsorption of Congo Red onto calcium-rich fly ash[4] and adsorption of basic red 2 onto peanut shell[15].

Effect of initial dye concentration on adsorption: Effect of initial dye concentration on adsorption was studied at five different concentrations of 20, 40, 60, 80 and 100 mg/L at 20 ºC and pH 9. Fig. 2 shows the effect of initial dye concentration on the adsorption of methyl violet by pirina. As shown in Fig. 2, a rapid adsorption occurs within the contact time of 5 min for all concentrations and thereafter the gradual increase in adsorption maintains to 90 min. While the amounts of methyl violet adsorbed onto pirina are 4.73 mg/g (94.46 %) and 9.28 mg/g (92.8 %), 12.80 mg/g (85.31 %), 17.14 mg/g (85.71 %) and 21.22 mg/g (84.86 %) for the initial concentrations of 20, 40, 60, 80 and 100 mg/L at 5 min, the maximum adsorption is found to be 4.76 mg/g (95.17%), 9.67 mg/g (96.67 %), 14.24 mg/g (94.92 %), 18.56 mg/g (94.29 %)

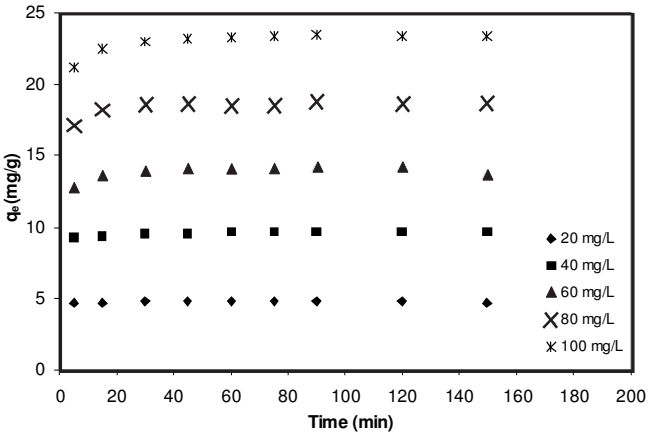

Fig. 2. Effect of initial concentration on adsorption of methyl violet by pirina

and 23.51 mg/g (94.03 %) at 90 min, respectively. The fact that the high adsorption occurs for the first minutes indicates a very high interaction between functional groups on the surface of modified pirina and methyl violet molecules. A similar result has been reported for the adsorption of basic red 2 onto peanut shell[15]. The very high interaction was also seen in pH and temperature studies.

Effect of pH on adsorption: The initial pH values of dye solutions affect both the chemistry of a dye molecule and an adsorbent. Herein, to investigate the effect of pH on the adsorption of methyl violet from aqueous solution by pirina, the pHs of initial solutions were selected as 3, 5, 7 and 9. For the initial concentration of 40 mg/L at 20 ºC, the relationship between the amounts of methyl violet adsorbed at equilibrium time and the initial solution pH is shown in Fig. 3. As shown in Fig. 3, a very rapid adsorption takes place for the first minutes at all the pHs as in concentration effect and thereafter the gradual increase in adsorption prosecutes up to 90 min, maximum adsorption time. The most adsorption occurs at pH 9 and the lower adsorption occurs at pH 3. When the adsorption is 1.86 mg/g (18.60 %) and 7.098 mg/g (70.98 %) at 5 and 90 min at pH 3, the adsorption is 92.80 mg/g (92.80 %) and 9.67 mg/g (96.67 %) at 5 and 90 min at pH 9, respectively.

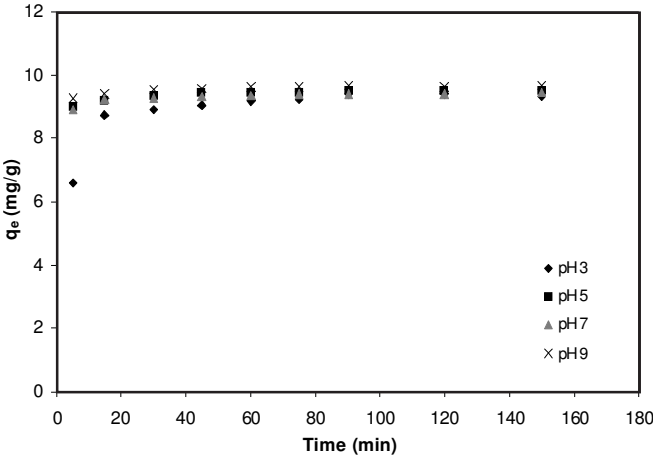

Fig. 3. Effect of initial solution pH on adsorption of methyl violet by pirina

Effect of temperature on adsorption: The effect of temperature on adsorption was studied at the temperatures of 20, 30, 40 and 50 ºC. The results obtained are showed in Fig. 4. As illustrated in the figure, a rapid adsorption is observed for the first minutes as seen in concentration and pH effects and then a gradual increase in adsorption is continued up to 90 min. While the highest adsorption occurs at 20 ºC at first 10 min, the lowest adsorption is resulted at 50 ºC. For example, for the initial concentration of 40 mg/L at 20 ºC, while the highest adsorption is 9.28 mg/g (92.80 %) at 5 min, the maximum adsorption is 9.67 mg/g (96.70 %) at 90 min. At 50 ºC, while the lowest adsorption is 7.34 mg/g (73.42 %) at 5 min, the maximum adsorption is 8.63 mg/g (86.36 %) at 90 min. The fact that the adsorption is the most at lower temperature indicates an exothermic process. Namely, the adsorption is more favourable in lower temperature. However, the maximum amounts of methyl violet adsorbed between 20 and 40 ºC are closed to each other, except 50 ºC. The adsorption at 50 ºC is lower than that of other temperatures.

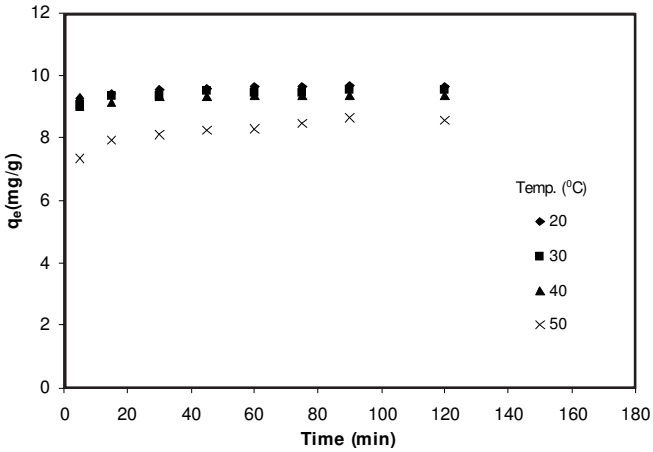

Fig. 4. Effect of solution temperature on adsorption of methyl violet by pirina

Effect of particle size on adsorption: The effect of particle size of adsorbent on adsorption was studied at the sizes of 45, 60, 80 and 100 mesh. The results obtained are showed in Fig. 5. As illustrated in the figure, it is seen that the adsorption increases with decreasing particle size to 45 from 100 mesh. This situation indicates the most adsorption as a result of increasing contact surface of adsorbent with lower particle size. The effect of particle size on adsorption is significantly observed for the first 30 min. After this time, as the adsorption is continued up to 90 min, the amounts of dye adsorbed are closed to each other. This may be attributed that the particles of the pirina may be turned into sludge with increasing contact time for 30-90 min, *i.e.*, between 30 and 90 min. For example, for the initial concentration of 40 mg/L at 20 ºC, the maximum adsorptions are found as 9.43 mg/g (94.30 %), 9.59 mg/g (95.90 %), 9.63 mg/g (96.30 %), 9.67 mg/g (96.70 %) for 45, 60, 80 and 100 mesh at 90 min, respectively.

Adsorption of methyl violet onto activated carbon: Effect of initial dye concentration on activated carbon adsorption was studied under same conditions as in adsorption performed by pirina, *i.e.*, at five different initial concentrations between 20 and 100 mg/L at 20 ºC and pH 9. For all concentrations, a very high adsorption is seen at first 1-2 min. Percentage of dye removed by activated carbon was determined

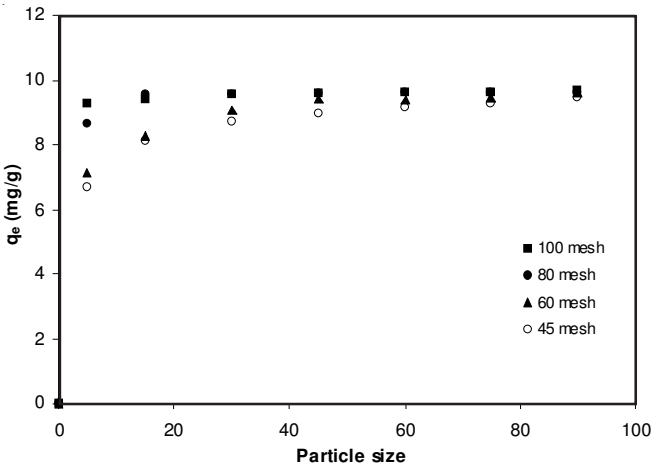

Fig. 5. Effect of particle size on adsorption of methyl violet by pirina

as 97-99 % between the initial concentrations of 20 and 100 mg/L. Moreover, it is seen that the violet colour of methyl violet turns to colourless within 1-2 min. This situation indicates also a very high affinity between activated carbon and methyl violet.

Ratio of solid activated carbon to liquid dye solution: As mentioned above, the amount of adsorption determined by using 2 g pirina and 500 mL dye solution onto activated carbon is found as 24.59 mg/g (98.37 %) and the adsorption is resulted at a very short time of 1-2 min. And therefore, adsorption experiment is done by decreasing the amounts of pirina. In case of ratio of solid to liquid with 0.5 g pirina/500 mL dye solution, the maximum amount of dye adsorbed is found to be 97.35 mg/g (97.35 %) within 1-2 min for the initial concentration of 100 mg/L and after contact time of 2 min, the amount of dye adsorbed is not almost change. In case of ratio of solid to liquid with 0.25 g pirina/500 mL dye solution, the amount of dye adsorbed is estimated to be 96.25 mg/g (96.25 %) for the initial concentration of 100 mg/L, but equilibrium time has gone up to 90 min. The maximum amount of dye adsorbed at 90 min is found to be 189.30 mg/g and its per cent is 94.65 %. The results are summarized in Table-1. As shown from the table, activated carbon is highly effective for the adsorption of methyl violet.

Comparison of experimental adsorption capacities of pirina to some sorbents: In this study, for all initial concentrations of methyl violet at pH 9 for a contact time of 90 min, the most adsorption is occurred at 20 ºC. The maximum amount of methyl violet adsorbed per unit pirina is 9.66 mg/g and its maximum percentage is 96.60 mg/g for pH 9 at 20 ºC. These values obtained for the adsorption of methyl violet onto pirina are compared to the adsorption of methyl violet by another sorbents under different conditions and they are presented in Table-1. The maximum amounts of dye adsorbed by various adsorbents in equilibrium time vary as a function of experimental conditions. Especially the amount of adsorbent dose has a very important effect on the estimation of the maximum amounts of dye adsorbed per unit adsorbent. As shown in Table-1, for example, when the mass of Pu-er tea cake used for the adsorption of methyl violet is 0.20 g (ratio adsorbent dose/solution = 2.0 g/L), the maximum amounts adsorbed per unit pu-er tea cake in equilibrium have been found as 42.50 mg/g and per cent adsorption is 95 %[16]. When the mass of of Halloysite nanotubes clay minerals used for the adsorption of methyl violet is 0.10 g (ratio adsorbent dose/solution = 2.0 g/L), the maximum amount of methyl violet adsorbed per unit Halloysite nanotubes clay minerals has been found as 24.91 mg/g and its percentage are 99.64 %[17]. In the present work, when the mass of Pirina used for the adsorption of methyl violet is 2 g (ratio adsorbent dose/solution = 4.0 g/L), the maximum amount of methyl violet adsorbed per unit pirina is 23.50 mg/g and per cent adsorption is 94.03 % for the initial concentration of 100 mg/L at pH 9 and 20 ºC. This indicates that the pirina will be a favorable adsorbent for the adsorption of methyl violet.

Adsorption isotherms: Adsorption isotherm analysis was performed using equilibrium data for the initial methyl violet concentrations of 40, 60, 80 and 100 mg/L. The adsorption equilibrium data obtained were fitted to Langmuir and Freundlich isotherms used commonly. Linearized Langmuir[4] and Freundlich[17,21] adsorption isotherms can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad (2)$$

where q_e is the amount of dye adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the dye in solution (mg/L). k and n are isotherm constants which indicate

TABLE-1
COMPARISON OF EXPERIMENTAL ADSORPTION CAPACITIES OF PIRINA TO SOME SORBENTS FOR METHYL VIOLET ADSORPTION

Capacity (mg/g) (%)	Experimental conditions (mg/g)	Biosorbent/adsorbent	Reference
9.66 (96.60)	C_o = 40 mg/L, T = 20 ºC, pH = 9, V = 500 mL, W = 2 g	Pirina	This study
23.50 (94.03)	C_o = 100 mg/L, T = 20 ºC, pH = 9, V = 500 mL, W = 2 g	Pirina	This study
24.59 (98.37)	C_o = 40 mg/L, T = 20 ºC, pH = 9, V = 500 mL, W = 2 g	AC	This study
97.35 (97.35)	C_o = 100 mg/L, T = 20 ºC, pH = 9, V = 500 mL, W = 0.5 g	AC	This study
189.30 (94.65)	C_o = 100 mg/L, T = 20 ºC, pH = 9, V = 500 mL, W = 0.25 g	AC	This study
42.50 (95.0)	C_o = 100 mg/L, T = 20 ºC, pH = 8, V = 100 mL, W = 0.20 g	Pu-er tea cake	16
(24.91 (99.64)	C_o = 50 mg/L, T = 25 ºC, pH = natural, V = 50 mL, W = 0.10 g	Halloysite nanotubes	17
89.12 (22.28)	C_o = 200 mg/L, T = 25 ºC, pH = natural, V = 50 mL, W = 0.10 g	Halloysite nanotubes	17
69.20 (73.0)	C_o = 472.7 mg/L (1.2×10^{-3} M), T = 30 ºC, pH = solution, V = 2 L, W = 5 g	Spiolite	18
32.60 (83)	C_o = 3.94 mg/L (1×10^{-5} M), T = 30 ºC, pH = 3, V = 25 mL, W = 0.10 g	Bottom ash	19
5.90 (74.87)	C_o = 78.80 mg/L (2×10^{-4} M), T = 30 ºC, pH = 9, V = 1 L, W = 10 g	Perite	20

C_o = Initial dye concentration (mg/L), T = Temperature, V = Solution volume, W = Adsorbent/biosorbent amount.

capacity and intensity of the adsorption, respectively. Q_o and b are Langmuir constants which indicate adsorption capacity and energy, respectively. The isotherm results indicate that the adsorption of methyl violet onto pirina is in consistent with the Langmuir and Freundlich models. Similar results have been reported for the adsorption of methyl violet onto Halloysite nanotubes clay minearlas[17] and Mansonia wood sawdust[22].

Fig. 6 shows the plot of C_e/q_e against C_e at 20 ºC and pH 9. The plot is in harmony with Langmuir model with a correlation coefficient of 0.90. Fig. 7 shows the plot of ln q_e against ln C_e at 20 ºC and pH 9. The plot obeys Freundlich model with a high correlation coefficient of 0.98. The values of Q_0 and b were calculated from the intercept and slope of the plot of C_e/q_e *versus* C_e, respectively. These constants (Q_0 and b) obtained from the Langmuir isotherm are found to be 40.49 mg/g and 0.172 g/L, respectively. The values of k and n were calculated from the intercept and slope of the plot of ln q_e *versus* ln C_e, respectively. The values k and n are found as 7.92 mg/g and 1.72 g/L, respectively.

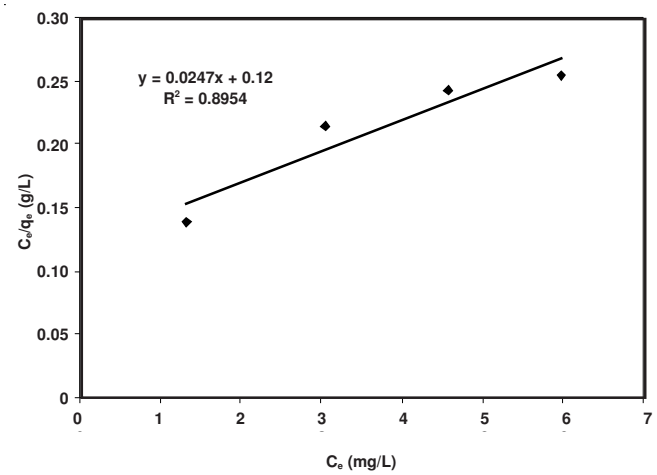

Fig. 6. Langmuir isotherm of adsorption of methyl violet by pirina

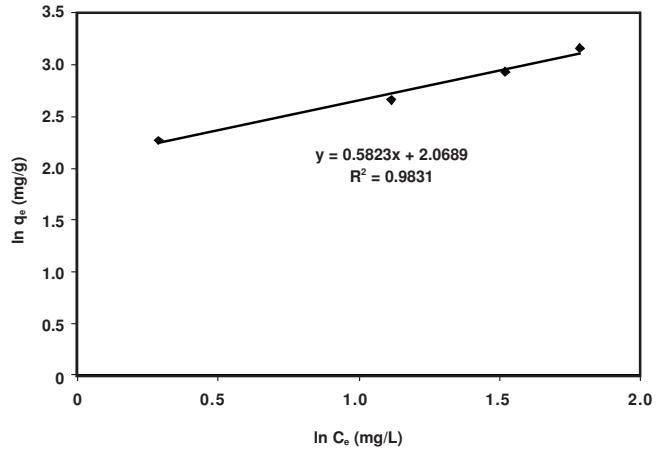

Fig. 7. Freundlich isotherm of adsorption of methyl violet by pirina

Moreover, original adsorption isotherm, *i.e.*, the maximum amount of dye adsorbed against concentrations remaining in equilibrium time, was also studied at 20 ºC, pH 9 and 400 rpm. The original isotherm obtained was shown in Fig. 8. It is evident from this figure that the adsorption is a lower energy

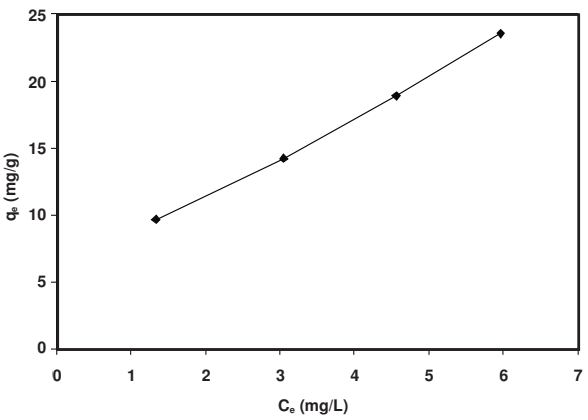

Fig. 8. Original adsorption isotherm of methyl violet removal by pirina

and physical process in terms of Giles *et al.*[23] classification. The fact that the adsorption indicates a physical process with a lower energy has also been evaluated *via* intra-particle diffusion kinetic and thermodynamic studies.

Intra-particle diffusion kinetics: An intra-particle diffusion model of Weber and Morris[24,25] is shown as

$$q_t = k_i \cdot t^{1/2} \quad (3)$$

where, k_i is intra-particle diffusion rate constant. q_t are the amount adsorbed of solute per unit adsorbent at any time. t is contact time.

Due to mass transfer effects, the plots of q_t *versus* $t^{1/2}$ for intra-particle diffusion model given in eqn. 3 were obtained for all initial dye concentrations at 20 ºC and pH 9. The plots for the intra-particle diffusion model are demonstrated in Fig. 9. If notice to this figure, it can be seen that the adsorption process tends to be followed by two phase. Phase I indicates from the bulk phase to adsorbent surface (*i.e.*, surface adsorption) and phase II points to intra-particle diffusion within particles of pirina. The calculated intra-particle diffusion rate constants are found to be 0.023, 0.054, 0.076, 0.091 mg/g $min^{1/2}$ for initial dye concentrations of 40, 60, 80 and 100 mg/L, respectively. The intra-particle diffusion of dye molecules is found to be rate controlling in the adsorption process after 0.5 h contact times. A similar result has been reported in a study entitled kinetic and mechanism of adsorption of methylene blue onto nitric acid treated water-hyacinth[26].

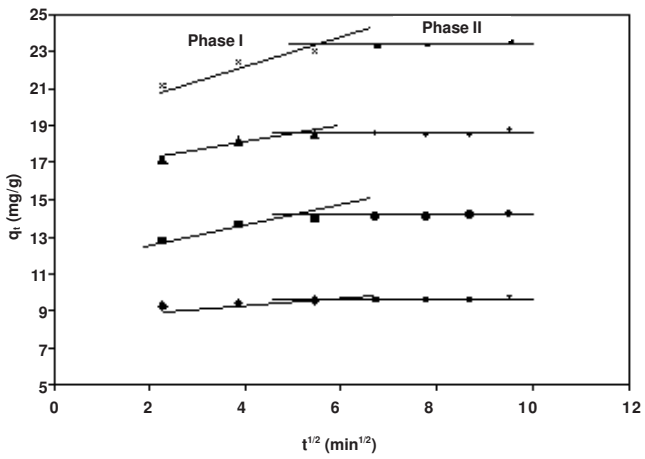

Fig. 9. Intra-particle diffusion kinetics of methyl violet adsorption by pirina at diffirent concentrations

Thermodynamic studies: The various thermodynamic parameters, *i.e*., standard free energy, standard enthalpy and standard entropy, related to the adsorption of methyl violet onto pirina were determined by using the following equations: In understanding better the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change, ΔG^o, standard enthalpy, ΔH^o and standard entropy, ΔS^o. The Gibbs free energy of adsorption by using equilibrium constant (K_c) is calculated from the following equation[27,28]:

$$\Delta G^o = -RT \ln K_c \quad (4)$$

The equilibrium constant K_c at various temperatures was determined from the following equation[29]:

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (5)$$

where, C_{Ae} and C_{Se} are the equilibrium concentrations of metal ions on the adsorbent (mg/L) and in solution (mg/L), respectively. Standard enthalpy, ΔH^o and standard entropy, ΔS^o, of adsorption can be estimated from von't Hoff equation given in the following[27,28]:

$$\ln K_c = \frac{-\Delta H^\circ_{ads}}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

where, R is the gas constant, K_c is adsorption equilibrium constant. The plot of ln K_c *versus* 1/T (in Kelvin) should be linear (Fig. 10). The slope of van't Hoff plot is equal to $-\Delta H^o_{ads}/R$ and its intercept is equal to $\Delta S^o_{ads}/R$. van't Hoff plot of the adsorption of methyl violet by pirina is shown in Fig. 10. Thermodynamic parameters obtained from van't Hoff plot for the adsorption of methyl violet onto the pirina are given Table-2. As shown in the table, the negative values of ΔG^o at different temperatures indicate the spontaneous nature of the adsorption process. Generally, the more negative of ΔG^o indicates the greater the driving force of the adsorption process, resulting in higher adsorption capacity. The plot of q_e against ΔG^o is shown in Fig. 11. It is seen from the figure that a good linear relation between q_e and ΔG^o is present. The maximum amount of methyl violet adsorbed is increased with decreasing free energy change. ΔH^o is found to be -3.92 kcal/mol, indicating the physical adsorption. Because, if heat of an adsorption process is <10 kcal/mol, it is a physical process[30]. Moreover, negative enthalpy indicates a decreasing adsorption with increasing temperature. Namely, the adsorption is in favour of decreasing temperature. The similar values of negative ΔG^o and ΔH^o have been for the bioadsorption of methyl violet onto Halloysite nanotubes clay minerals[17]. Also ΔS^o is found as -9.63 cal/mol K. The negative value of ΔS^o indicates that the pirina has a high affinity to the adsorption of methyl violet molecules. A similar result of negative ΔS^o has been reported for the adsorption of remazol red B onto activated carbon prepared from olive stone with $ZnCl_2$ treatment[31].

TABLE-2
THERMODYNAMIC PARAMATERS FOR METHYL VIOLET ADSORPTION ONTO PIRINA

Temperature (ºC)	q_e (mg/g)	ΔG^o (cal/mol)	ΔH^o (cal/mol)	ΔS^o (cal/mol K)
20	9.66	-1961	-3918	-9.63
30	9.53	-1815		
40	9.37	-1682		
50	8.63	-1185		

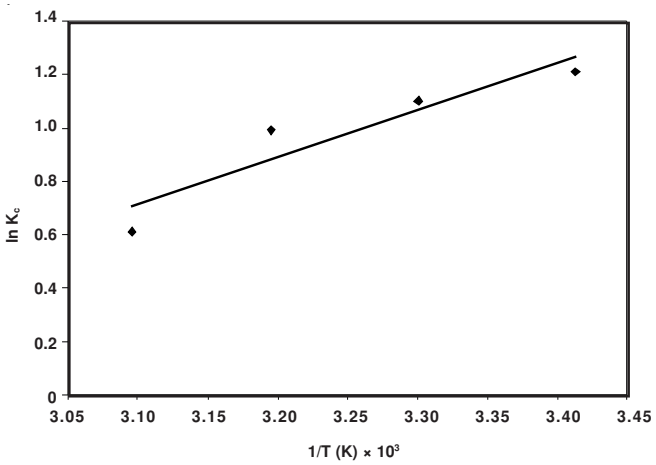

Fig. 10. van't Hoff plot of the adsorption of methyl violet by pirina

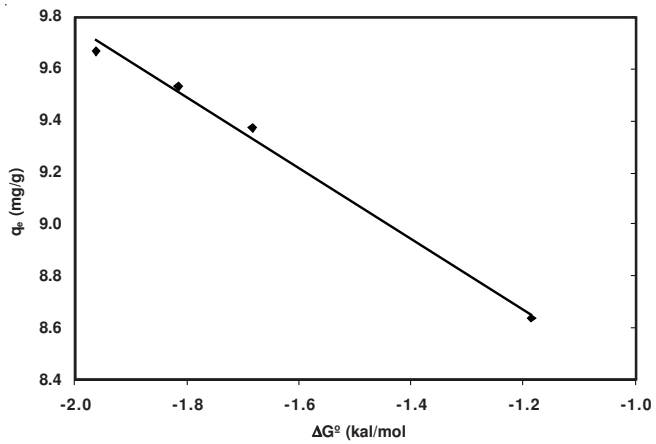

Fig. 11. Plot of amount of methyl violet adsorbed by pirina (q_e) against ΔG° for methyl violet onto pirina

Conclusion

Pirina, a waste of olive oil factory, was used as an adsorbent for the removal of methyl violet from aqueous solution by adsorption technique. The adsorption of methyl violet was investigated as a function of initial dye concentration, pH, temperatures and particle size. It was determined that the maximum adsorptions were between 82.14 and 97.42 % under all the experimental conditions studied. The values of adsorption obtained from column experiments were between 98.03 and 100 % for all concentrations. Adsorption isotherm was in consistent with the Langmuir and Freundlich model. The maximum amount of methyl violet adsorbed onto activated was found to be 189.30 mg/g per unit adsorbent. Per cent adsorption obtained onto activated carbon used between 0.25 and 2.00 g was changed between 94 and 99 %. The kinetics of adsorption followed the intra-particle diffusion model. From the thermodynamic studies, it was determined that the adsorption process was of spontaneous and exothermic nature. From the results reported it would appear that pirina can be used as a potential adsorbent for dye removal from industrial wastewaters.

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REFERENCES

1. Q.H. Hu, S.Z. Qiao, F. Haghseresht, M.A. Wilson and G.Q. Lu, *Ind. Eng. Chem. Res*., **45**, 733 (2006).
2. M. Dogan and M. Alkan, *J. Colloid Interf. Sci*., **267**, 32 (2003).
3. P. Nigam, G. Armour, I.M. Banat, D. Singh and R. Marchant, *Bioresour. Technol*., **72**, 219 (2000).
4. B. Acemioglu, *J. Colloid Interf. Sci*., **274**, 371 (2004).
5. Y.S. Ho and G. McKay, *Chem. Eng. J*., **70**, 115 (1998).
6. B. Acemioglu, *Chem. Eng. J*., **106**, 73 (2005).
7. H.M. Asfour, O.A. Fadali, M.M. Nassar and M.S. El-Geundi, *J. Chem. Technol. Biotechnol*., **35A**, 21 (1985).
8. B. Acemioglu, M. Kertmen, M. Digrak, M.H. Alma, *Afr. J. Biotechnol*., **9**, 874 (2010).
9. M. Ugurlu, A. Gurses and M. Acikyildiz, *Micropor. Mesopor. Mater.*, **111**, 228 (2008).
10. Ö. Görel, E. Emrullah, I. Doymaz, N.A. Akgün, Zeytinyagi Fabrika Atiklarinin Degerlendirilmesi, Yildiz Teknik Üniversitesi, Kimya Mühendisligi Bölümü, Kimya Teknolojileri Sayi, 26 (2003) (in Turkish).
11. A. Aziz, M.S. Oualia, H. Elandaloussia, L.C Menorval and M. Lindheimer, *J. Hazard. Mater*., **163**, 441 (2009).
12. G. Cimino, R.M. Cappello, C. Caristi and G. Toscano, *Chemosphere*, **61**, 947 (2005).
13. I. Kula, M. Ugurlu, H. Karaoglu and A. Celik, *Bioresour. Technol*., **99**, 492 (2008).
14. P. Galiatsatou, M. Metaxas and V. Kasselouri-Rigopoulou, *J. Hazard. Mater*., **B91**, 187 (2002).
15. N. Sakalar, M.H. Bilir, B. Acemioglu and M.H. Alma, *Asian J. Chem*., **22**, 5649 (2010).
16. P. Li, Y.J. Su, Y. Wang, B. Liu and L.M. Sun, *J. Hazard. Mater*., **179**, 43 (2010).
17. R. Liu, B. Zhang, D. Mei, H. Zhang and J. Liu, *Desalination*, **268**, 111 (2011).
18. M. Dogan, Y. Ozdemir and M. Alkan, *Dyes Pigm*., **75**, 701 (2007).
19. A. Mittal, V. Gajba and J. Mittal, *J. Hazard. Mater*., **150**, 364 (2008).
20. M. Dogan and M. Alkan, *Chemosphere*, **50**, 517 (2003).
21. Y.C. Wong, Y.S. Szeto, W.H. Cheung and G. McKay, *Process Biochem*., **39**, 695 (2004).
22. A.E. Ofomaja and Y.S. Ho, *Bioresour. Technol*., **99**, 5411 (2008).
23. C.H. Giles, T.H. MacEman, S.M. Nakhawa and D. Simith, *J. Chem. Soc*., **3**, 3973 (1960).
24. W.J. Weber and J.C. Morris, *J. Sanit Eng. Div.*, **89**, 31 (1963).
25. N. Kannan and M.M. Sundaram, *Dyes Pigm*., **51**, 25 (2001).
26. M.I. El Khaiary, *J. Hazard. Mater*., **147**, 28 (2007).
27. M. Hema and S. Arivoli, *Int. J. Phys. Sci*., **2**, 10 (2007).
28. B. Acemioglu, *Bioresour. Technol.*, **93**, 99 (2004).
29. B. Acemioglu and M.H. Alma, *J. Colloid Interf. Sci*., **243**, 81 (2001).
30. M.B. McBride, Environmental Chemistry of Soils, Oxford University, Inc. Oxford (1994).
31. M. Ugurlu, A. Gurses and C. Dogan, *Color Technol*., **123**, 106 (2007).