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RESEARCH ARTICLE

Adsorption of methyl red on local kaolin from spiked aqueous solution

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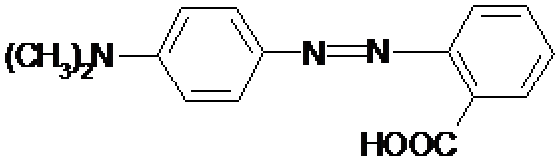
Abstract:
Presence of colour in natural water is aesthetically undesirable. It retards growth of aquatic organisms. However, the soil serves as an important filtering medium for scavenging coloured substances and other pollutants from industrial effluents and runoff waters. The clay component of soil plays a significant role in this case. Considering the possible harmful effects of methyl red in water, a study was conducted for removal of the synthetic dye from spiked aqueous solution by adsorption on Kaolin. The kaolin-dye interaction was studied under laboratory conditions with respect to kaolin obtained from local sources. Kaolin was used in six different forms. The effect of methyl red concentration, amount of kaolin, pH, temperature and time was investigated. The results indicate that kaolin can be very effective in removing an acidic dye like methyl red from water. The pure kaolin showed the highest adsorption capacity. The raw kaolin itself showed considerable adsorption of 43 – 58%. Optimum adsorption occurred between pH 3.0 and 4.0. Thermal treatment of kaolin resulted in reduction of adsorption capacities while treatment with NaOH enhanced the same. The adsorption data fitted Freundlich and Langmuir adsorption isotherms. Computation of thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 showed that the adsorption of methyl red on kaolin was a favourable and spontaneous process. The process of adsorption was found to follow simple first order kinetics.

Keywords: kaolin, adsorption of acidic dye, methyl red.

Introduction

Kaolin is a hydrous aluminum silicate of the approximate composition $2H_2O.Al_2O_3.2SiO_2$. Kaolin has a low cation exchange capacity and is not rated as a good ion exchanger. However kaolin is an important constituent of soil and therefore its role as a scavenger of contaminants from water needs to be investigated. Kaolin has no inter layer exchange sites and also it has no structural charge imbalance. Still it is shown to have some amount of surface reactivity. Adsorption is a widely investigated technique for treating contaminated water. Various adsorbents are used to remove dyes and coloured substances from water. The present work aims to elucidate the interactions between kaolin and methyl red in aqueous solution.

Methyl red is a synthetic dye of chemical formula, $[(CH_3)_2NC_6H_4N{=}NC_6H_4CO_2H]$, and chemical name 2-[4-(dimethylamino) phenyl azo] benzoic acid with the structure below:



Methyl red, if enters into the body by inhalation, ingestion, or by absorption through skin, may affect the central nervous system, cause liver and kidney damage. It is regarded as a poisonous substance, which may also cause blindness if swallowed. Its vapours are harmful to the eyes, can cause irritation and painful sensitization to light. Ingestion is also likely to cause digestive tract irritation, respiratory failure, cardiovascular collapse, and kidney failure and severe depression. Chronic exposure to small amounts can cause dermatitis. Prolonged or repeated contact with methyl red may cause dryness, cracks and irritation on the skin. In animals, methyl red has adverse reproductive and foetal effects.

The azo dyes are the largest and most versatile of all dyes used in the textile and dyeing industries and they are characterized by the presence of one or more azo groups [-N=N-] in association with one or more aromatic rings (Gordon and Gregory 1983). The azo dyes are relatively resistant to biological and chemical degradation in addition to their being toxic and/or carcinogenic (Anliker 1979, Chung et al. 1981, Holme 1984). Methyl red is also a synthetic azo dye. It is therefore essential that any effluent containing an azo dye like methyl red must not be discharged into natural water bodies without prior treatment.

2. Experimental

The adsorbent for the experiment were collected in in bright white lumps from the Silonijan area (Karbi-Anglong district, Assam, India). After collection, the samples were washed repeatedly with water to remove stones, sand and other heavy materials. The lumps were crushed, ground and sieved through a 230-mesh sieve for removing the large non-clay fractions for obtaining raw kaolin (C1). A part of the raw kaolin was kept suspended in double distilled water in a 1-liter beaker for several hours and then the mixture was stirred with addition of small amounts of 30% hydrogen peroxide solution to remove organic substances till all effervescence ceased. The mixture was kept overnight, the clear liquid was decanted from the top, more water was added, stirred, and allowed to settle down for 3 – 4 hours. The clear liquid at the top was removed carefully and the process was repeated several times to get rid of excess hydrogen peroxide solution. After adding more water, the mixture was agitated vigorously for some time and the suspended kaolin was kept in wide glass plates in an air oven at around 343 K for slow evaporation to dryness (Moore and Reynolds, 1989) to obtain pure kaolin (C2).

Chemical analysis followed by XRD and IR measurements showed the samples to be very high purity kaolin, almost similar to kaolin sample (KGa-1b) obtained from University of Missouri-Columbia, Source Clay Minerals Repository, Columbia. Samples of both raw and pure kaolin were heated at 770K for 6 hours to obtain thermally treated raw kaolin (C3) and pure kaolin (C4). To prepare NaOH-treated kaolin, 6g each of raw and pure kaolin was agitated with 100 ml 1M NaOH for 4 hours in a mechanical shaker, left overnight, filtered, and washed with water. The residue was dried at 350 K to obtain NaOH-treated raw kaolin (C5) and pure kaolin (C6). Methyl Red (Ranbaxy Laboratories, India) was used as the adsorptive without any further purification.

Although the dye is not much soluble in water, a stock solution containing 100 mg of methyl red in 1 dm^3 of double distilled water could be prepared from which solutions of different concentrations were made.

Adsorption studies were carried out in a batch process. 25 ml of methyl red solution in a stoppered 150 ml conical flask was shaken in a water bath thermostat with a given amount of the kaolin under different sets of conditions. As the adsorption was found to reach equilibrium in 2 hours, the contact time was fixed at 3 hours in all the sets. The pH of the adsorptive solution was altered by addition of dilute NaOH or dilute HCl. The mixture was centrifuged after adsorption and the unadsorbed methyl red was determined spectrophotometrically (Hitachi 3210). For calculation of adsorption parameters, Freundlich and Langmuir isotherms were used:

(a) Freundlich Isotherm:
$x/m = KC_e^n$ (1)

where x is the amount (mg) of dye adsorbed on m g of adsorbent at a particular temperature, C_e is the equilibrium concentration of the dye (mg/dm^3) and, K and n are Freundlich coefficients. n is usually < 1 for favourable adsorption. The linear form of Freundlich isotherm, i.e. $\log x/m = n \log C_e + \log K$ was used to compute the values of n and K.

(b) Langmuir equation:
$C_e/(x/m) = 1/(ab) + (1/b)C_e$ (2)

where x/m and C_e have the same meaning as in equation (1) above. From the linear plot of $C_e/(x/m)$ vs. C_e, the constants a and b are computed. In equation (2), the left-hand side represents the reciprocal fractional coverage, i.e.$1/\theta$ where θ gives the fraction of the adsorbent surface covered with the adsorptive molecules. The Langmuir constant b represents the monolayer coverage, i.e. the amount required to completely cover unit mass of the adsorbent with a monolayer. The Langmuir constant, a, is related to the equilibrium constant for the equilibrium between kaolin and the dye. Another dimensionless equilibrium parameter, R_L (Hall et al., 1966), is computed from the relation

$$R_L=/(1+aC) \qquad (3)$$

where a is the Langmuir constant and C is any adsorbate concentration at which the adsorption is carried out. For favourable adsorption, R_L should remain between 0 and 1 ($0< R_L <1$). The standard Gibbs energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated from the adsorption experiments carried out at different temperatures using the following equations (Khan et al., 1995):

$$\text{(a)}\log K_d=\Delta S^o/(2.303R)-\Delta H^o/(2.303RT) \qquad (4)$$
$$\text{(b)}\Delta G^0=\Delta H^0-T\Delta S^0 \qquad (5)$$
$$\text{(c)}K_d=(x/m)/(y/u) \qquad (6)$$

where K_d is the distribution coefficient for the adsorptive and is equal to the ratio of the amount adsorbed per unit mass (x/m in mg g^{-1}) to the adsorptive concentration in unit volume (y/u in mg dm^{-3}, y is the amount in mg of the adsorptive present in u dm^3 of solution). ΔS^0 and ΔH^0 are calculated from the plots of log K_d vs. 1/T and ΔG^0 is found from equation (5).

The time dependence of the adsorption process was studied by carrying out the adsorption experiments at constant temperature using fixed kaolin dose and fixed adsorptive concentration. The kinetics of adsorption was tested on the basis of the simple Lagergren equation (Trivedi et al., 1973):

$$\log (q_e - q) = \log q_e - k_{ad} . t/(2.303) \qquad (7)$$

where q_e is the amount adsorbed at equilibrium in mg g^{-1}, q is the amount adsorbed at time t in mg g^{-1}, k_{ad} is the adsorption rate constant in min^{-1}, and t is the adsorption time in min. Plot of log (q_e – q) vs. t gives a straight line for first order adsorption kinetics.

3. Results and Discussion

In all adsorption experiments six different adsorbents were used:

C1 – raw kaolin,
C2 – pure kaolin,
C3 – calcined raw kaolin,
C4 – calcined pure kaolin,
C5 – NaOH-treated raw kaolin, and
C6 – NaOH-treated pure kaolin

The cation exchange capacity (CEC) of the kaolins were estimated by the conventional $BaCl_2$ method and was found to be 2.62(C1), 2.85(C2), 1.94(C3), 3.08(C4), 2.17(C5) and 2.42(C6)meq/100g.The pure kaolin and its calcined sample have higher CEC compared to the other samples. Calcination improved the CEC of the pure kaolin while that of the raw kaolin decreased. The treatment with NaOH decreased the CEC of the raw and the pure kaolin.

The six different kaolin samples adsorb methyl red to different extents. At a constant adsorbent dose, the adsorption of methyl red at 303 K was maximum for the pure kaolin (C2). The raw kaolin (C1) showed much less adsorption compared to the pure kaolin. The thermal treatment of both raw and pure kaolin (C3 and C4) resulted in a reduction of adsorption, while treatment with NaOH enhanced adsorption for the raw kaolin (C5), but decreased the same for the pure kaolin (C6). These results are shown in Figure 1 for six different initial concentrations of methyl red solution. The order of adsorption for the six clays was C2>C4>C6>C5>C1>C3.

The raw kaolin itself had considerable adsorption capacity. For example, 0.8 g of raw clay could remove more than 58 mg of methyl red from 1 dm^3 of aqueous solution. This improved to nearly 76.5% for the pure kaolin. The thermally treated raw and pure kaolin samples showed 52.5 and 72.1 % adsorption respectively. Treatment with NaOH improved adsorption of methyl red from 58 to 62 % for the raw kaolin, but the same treatment resulted in a decrease of adsorption from 76.6% to 65.5% for the pure kaolin. Purification of the raw kaolin through removal of organic matter with hydrogen peroxide treatment thus resulted in an increase in the number of adsorption sites for methyl red. Thermal treatment on the other hand decreased the number of sites. However, the raw and pure kaolin samples behave differently after NaOH treatment. The treatment appeared to have enhanced the number of methyl red adsorption sites in case of raw kaolin while substantially decreasing the same for pure kaolin, even more than that brought about by thermal treatment.

An increase in kaolin dose (Figure 2) showed a marked enhancement of adsorption for pure (C2) and thermally treated pure kaolin (C4). The results indicate that a large adsorbent dose was required in case of the adsorbents C1, C3, C5 and C6 for cent percent removal of methyl red from aqueous solution. However, the pure kaolin (C2) and its thermally treated form (C4) could remove as much as 95% and 89% of the adsorptive with a relatively small dose of 3.2 g dm^{-3} from water spiked with 20mg methyl red per dm^3. The gradually increasing adsorption followed the order C2>C4>C6>C5>C1>C3. This is in agreement with the observation that purification of kaolin improved the adsorption of methyl red.

The methyl red adsorption on kaolin depended on pH of the medium (Figure 3). The experiments could not be carried out above pH 6.0 as methyl red changed colour and λ_{max} shifted. The influence was more prominent for the adsorbents C2 (pure kaolin) and C6 (NaOH-treated pure kaolin). A gradual increase in adsorption was observed for all the kaolin samples from pH 2.0 to 3.5 after which a slow decrease was seen. The optimal pH range for adsorption of methyl red was observed to be between 3.0 and 4.0.

The adsorption data for all the six kaolin samples fitted both Freundlich and Langmuir isotherms (Figures 4 and 5). The adsorption constants derived from these isotherms are given in Table 1. The values of the Freundlich coefficient n were <1, in conformity with one of the essential conditions for favourable adsorption. The other Freundlich coefficient K had values in agreement with the trend of values of n. Pure kaolin (C2) and thermally treated pure kaolin (C4) had the highest values for both n and K.

The adsorbents, C2 and C4, had also the highest values for the Langmuir constant, b (64.10 and 60.98 mg g^{-1}, respectively). The other Langmuir constant, a, did not exhibit a clear trend. The highest values in this case were shown by raw kaolin (C1) and NaOH-treated pure kaolin (C6), while the other adsorbents had about half the value of that for these two. The dimensionless constant R_L (Itaya et al. 1984, McConvey and McKay 1985) yielded values (Table 1) in the range of 8.8 x 10^{-3} to 2.1 x 10^{-2}. These values indicate a favourable adsorption of methyl red on kaolin. Effect of temperature on the adsorption equilibrium between methyl red and the kaolin samples was studied at four different temperatures of 303, 308, 313 and 318 K (Figure 6). The adsorption decreased with increasing temperature showing the process to be exothermic in nature.

The thermodynamic parameters ΔS^0, ΔH^0 and ΔG^0 for the adsorption process were calculated from the plots of log K_d vs. 1/T (Table 2). The three thermodynamic parameters yielded values indicating thermodynamically favourable, spontaneous adsorption of methyl red on kaolinite. The standard enthalpy change, ΔH^0, was negative in all the cases, the average values of the six adsorbents being in the range – 6.22 to – 24.44 kJ mol^{-1}. The thermally treated pure clay (C4) and the pure clay (C2) itself had higher ΔH^0 values compared to the other adsorbents, which had ΔH^0 around – 6.0 to – 7.0 kJ mol^{-1}. The standard entropy change, ΔS^0, yielded small positive values in all the cases within the range 9.7 to 30.8 J K^{-1} mol^{-1}. The positive values indicate that kaolin-methyl red equilibrium was reached spontaneously. The small entropy change accompanying the adsorption process showed that the adsorption of methyl red on the clay surface did not bring about major structural change although small increases in disorder in arranging the methyl red molecules on the kaolin surface was possible. The standard Gibbs energy change, ΔG^0 remained between – 14.15 to – 15.79 kJ mol^{-1} indicating that the adsorption process brought about a considerable decrease in Gibbs energy.

The kinetics of methyl red adsorption was studied with respect to raw (C1) and pure (C2) kaolin samples at 303 K by varying the contact time from 10 to 180 minutes. The variation of adsorption with time is shown in Figure 7. Adsorption was practically over within 10 minutes although the equilibrium took almost 2 hours to attain. A similar study with methyl red as the adsorptive could not be found in the literature. However, in case of acid brown dye, Sekaran et al. (1995) have found that adsorption equilibrium was attained in 60 minutes with a leather industry waste as the adsorbent. Mall and Upadhyay (1995, 1998) observed that maximum removal of methylene blue by adsorption on boiler bottom ash occurred within 30 minutes although equilibrium was attained in about 4 hours. For adsorption of a number of basic dyes on chemically treated leaves, Singh and Srivastava (1999) found that 87% of the adsorption was complete within 30 minutes, but the equilibrium was reached only after 180 minutes. The adsorption of methylene blue on activated carbon, confirmed with Freundlich and Langmuir isotherm model,attains equilibrium with in 45 to 60min.(K. Manickavasakam, S. Madhava Krishnan, Y. sameena, N.Vennilamani and S. Pattabhi,2004).

The linear Lagergren plots [log (q_e – q) vs. t], shown in Figure 8 indicated that the adsorption of methyl red on kaolin (both raw and pure) followed simple first order kinetics. The first order rate constants (k_{ad}) evaluated from these plots had the values 5.04 x 10^{-2} min^{-1} (raw kaolin) and 5.07 x 10^{-2} min^{-1} (pure kaolin) showing that kaolin-methyl red interactions were moderately fast. Sekaran et al. (1995) obtained a value of 5 x 10^{-2} min^{-1} at 303 K for the rate constant of adsorption of acid brown dye on a solid waste, which was comparable to the value obtained in this work. On the other hand, Singh and Srivastava [1999] obtained values of 1.35 x 10^{-2} min^{-1} and 1.5 x 10^{-2} min^{-1} respectively for methylene blue and malachite green adsorption on chemically treated Psidium Guyava leaves at 303 K. The same two dyes, yielded k_{ad} values of 1.51 x 10^{-2} min^{-1} and 2.01 x 10^{-2} min^{-1} respectively for their adsorption at 303 K on boiler bottom ash (Mall and Upadhyay 1995). The agreement with first order kinetics and the k_{ad} values indicate that methyl red adsorption on kaolin was independent of the initial concentration of the dye. The adsorption process was very fast initially, but after saturating most of the surface sites, the adsorption became slow due to diffusion into the interior. Therefore, although the maximum amount of adsorption occurred within a few minutes, the equilibrium was attained only after a considerable length of time.

Ghosh and Bhattacharyya [2002] have reported ΔH, ΔS and ΔG values in the ranges of 6.03 to 13.53 kJ mol^{-1}, 69.69 to 88.16 J mol^{-1} K^{-1}, and –13.85 to –15.61 kJ mol^{-1}

respectively for endothermic adsorption of Methylene Blue on similer six kaolinite-based adsorbents. Endothermic uptake of the neutral dye, Congo Red on activated carbon made from coir pith was observed by Namasivayam and Kavitha [2002] with ΔH value of 7.71 kJ mol^{-1}.

The adsorption of the basic dye, Brilliant Green on Neem leaf powder was also found to be endothermic in nature with mean ΔH, ΔS, ΔG values of 12.12 kJ mol^{-1}, 67.02 J mol^{-1} K^{-1}, and –8.64 kJ mol^{-1}, respectively Bhattacharyya K G, Sarma A. [2003]. These values are

Table 1
Freundlich and Langmuir adsorption coefficients for adsorption of aqueous methyl red on kaolin at 303 K.

Kaolin sample	Freundlich n	Freundlich K (dm^3 g^{-1})	Langmuir a (dm^3 g^{-1})	Langmuir b Mg g^{-1}	R_L
C1	0.423	21.28	6.42	19.46	0.0088
C2	0.742	81.26	3.00	64.10	0.019
C3	0.546	22.36	3.38	23.15	0.0165
C4	0.744	69.23	2.60	60.98	0.0214
C5	0.504	28.00	5.04	25.13	0.0112
C6	0.500	30.66	5.33	26.81	0.0106

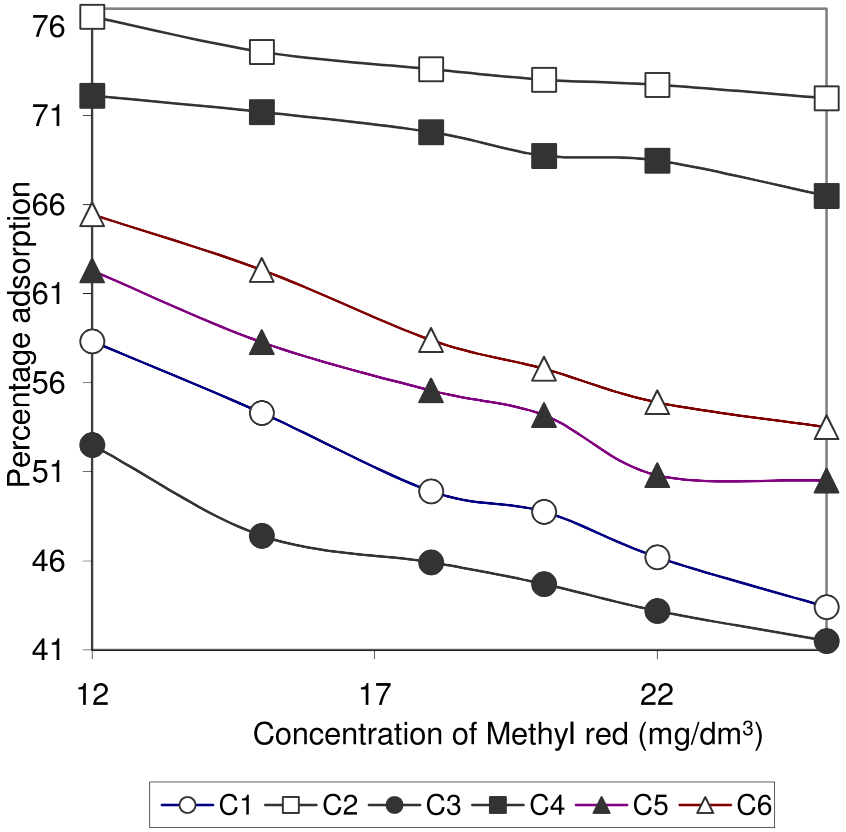


Figure1. Effect of adsorptive concentration [kaolin dose 0.8 g/dm^3, temperature 303 K, pH 5.0, contact time 3 hours]

Table 2
Thermodynamic data for adsorption of Methyl Red on kaolin [contact time 3 hours, methyl red concentration 20 mg dm^{-3}, pH 5.0].

	Clay dose			ΔS^0		$-\Delta G^0$				
Clay	g/L	Values	Mean	Values	Mean	303K	308K	313K	318K	Mean
C1	1.2	9.81	7.08	18.03	22.92	15.27	15.36	15.45	15.54	14.19
	1.6	7.84		22.37		14.62	14.73	14.84	14.95	
	2.0	7.20		22.76		14.10	14.21	14.32	14.44	
	2.4	6.05		25.20		13.69	13.81	13.94	14.06	
	2.8	5.79		24.98		13.36	13.48	13.61	13.73	
	3.2	5.78		24.15		13.10	13.22	13.34	13.46	
C2	1.2	16.48	12.78	0.63	9.71	16.67	16.67	16.68	16.68	15.79
	1.6	16.97		3.01		17.88	17.90	17.91	17.93	
	2.0	14.26		4.25		15.55	15.57	15.59	15.61	
	2.4	11.18		12.91		15.09	15.16	15.22	15.29	
	2.8	9.81		16.24		14.73	14.81	14.89	14.97	
	3.2	7.97		21.22		14.40	14.51	14.61	14.72	
C3	1.2	7.46	6.90	25.53	23.34	15.20	15.32	15.45	15.58	14.15
	1.6	7.99		21.74		14.58	14.69	14.80	14.90	
	2.0	7.29		22.30		14.05	14.16	14.27	14.38	
	2.4	6.69		22.93		13.64	13.75	13.87	13.98	
	2.8	6.03		24.10		13.33	13.45	13.57	13.69	
	3.2	5.96		23.46		13.07	13.19	13.30	13.42	
C4	1.2	32.41	24.44	53.05	30.81	16.34	16.07	15.81	15.54	14.87
	1.6	32.15		54.26		15.71	15.44	15.17	14.90	
	2.0	26.99		38.99		15.18	14.98	14.79	14.59	
	2.4	20.52		19.18		14.71	14.61	14.52	14.42	
	2.8	17.72		10.64		14.50	14.44	14.40	14.34	
	3.2	16.84		8.75		14.19	14.15	14.10	14.06	
C5	1.2	8.46	6.22	22.96	26.05	15.42	15.53	15.65	15.76	14.31
	1.6	9.62		16.92		14.75	14.83	14.92	15.00	
	2.0	4.92		30.50		14.16	14.31	14.47	14.62	
	2.4	4.73		29.73		13.74	13.89	14.04	14.18	
	2.8	4.95		27.88		13.40	13.54	13.68	13.82	
	3.2	4.63		28.29		13.20	13.34	13.49	13.63	
C6	1.2	8.25	6.79	24.46	25.07	15.66	15.78	15.91	16.03	14.58
	1.6	9.44		18.26		14.97	15.06	15.16	15.25	
	2.0	6.81		25.23		14.46	14.58	14.71	14.83	
	2.4	5.15		29.25		14.01	14.16	14.31	14.45	
	2.8	4.70		29.74		13.71	13.86	14.01	14.16	
	3.2	6.40		23.49		13.52	13.64	16.75	13.87	

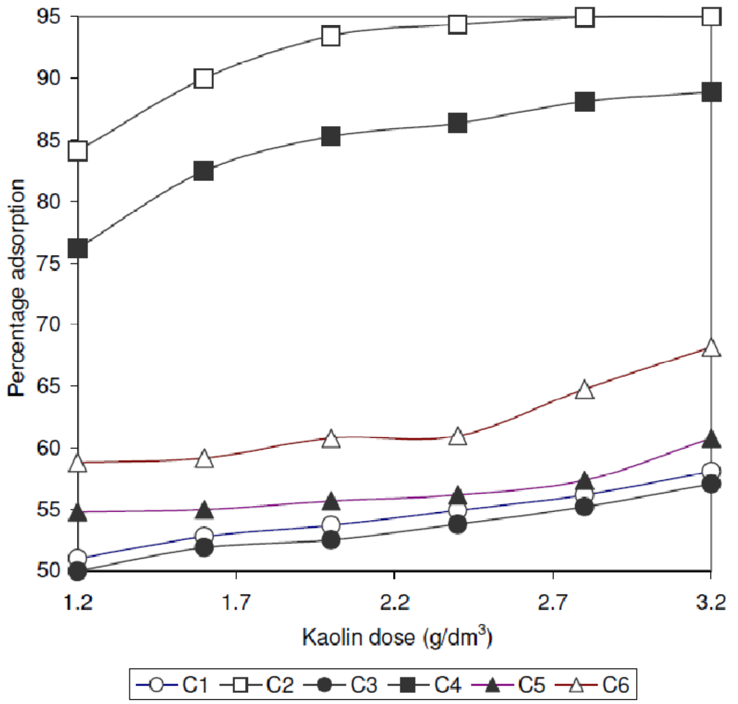


Figure 2. Effect of clay dose on methyl red adsorption on clays [methyl red concentration 20 mg/dm^3, pH 5.0, temperature 303 K, contact time 3 hours].

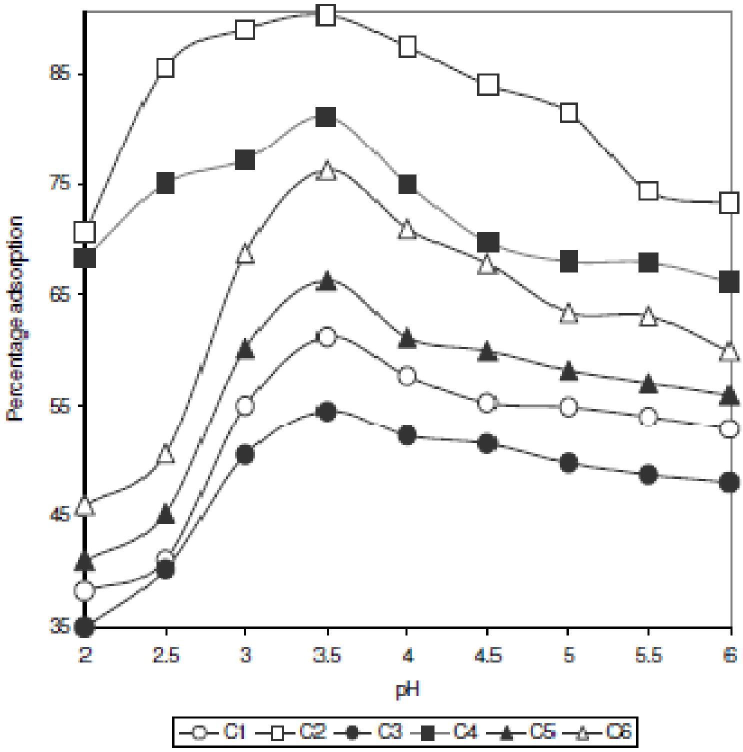


Figure 3. Influence of pH on adsorption of methyl red on kaolin [kaolin dose 0.8 g/dm^3, methyl red concentration 20 mg/dm^3, temperature 303 K, contact time 3 hours].

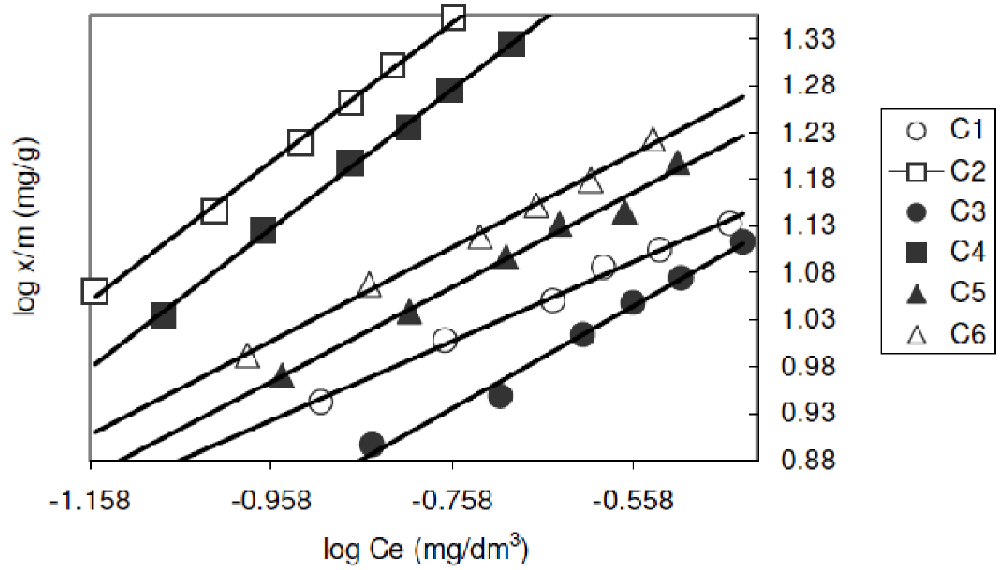


Figure 4. Freundlich adsorption isotherms for adsorption of methyl red on kaolin at 303 K.

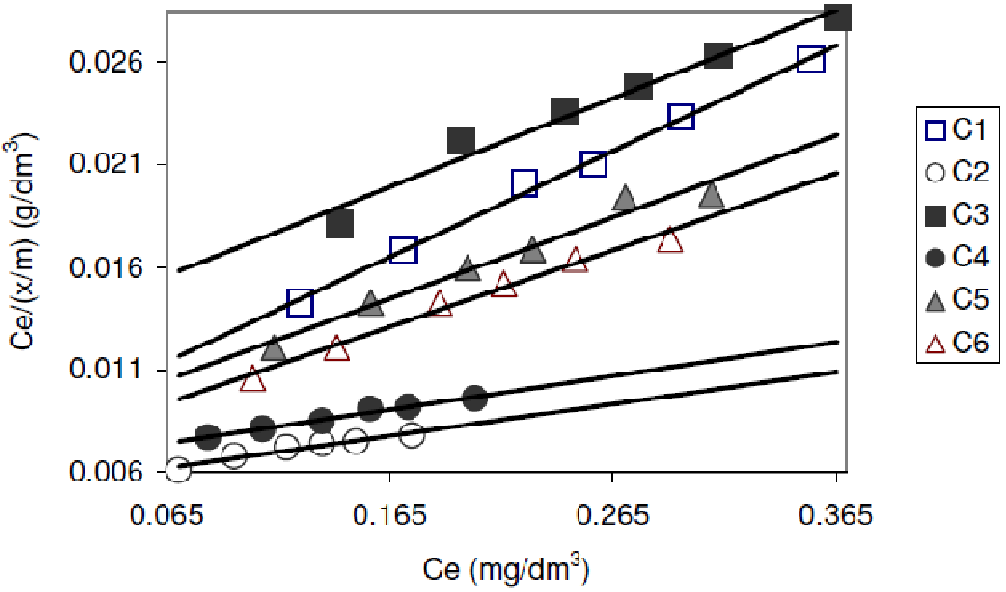


Figure.5. Langmuir adsorption isotherms for adsorption of methyl red on kaolin at 303 K

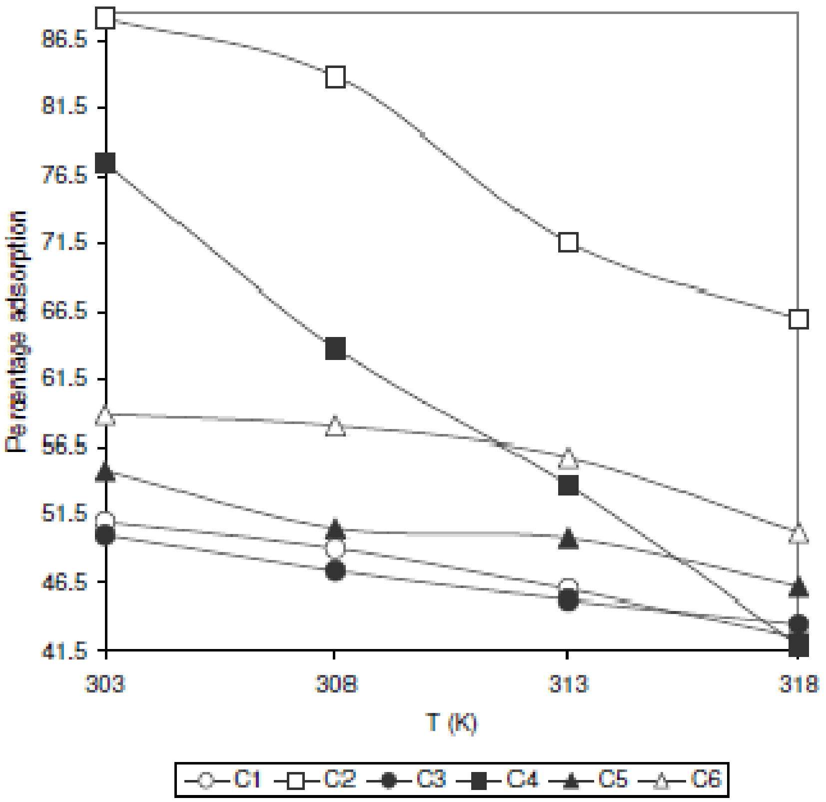


Figure.6. Effect of temperature on adsorption of methyl red on kaolin [kaolin dose 1.2 g/dm^3, methyl red concentration 20 mg/dm^3, pH 5.0, contact time 3 hours].

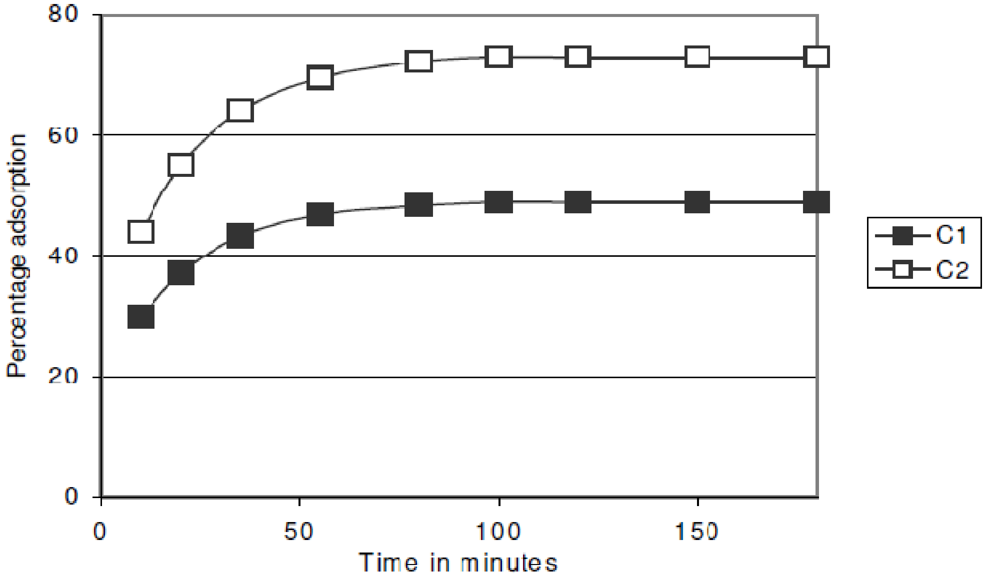


Figure 7. Variation of adsorption with time for raw (C1) and pure (C2) kaolin.

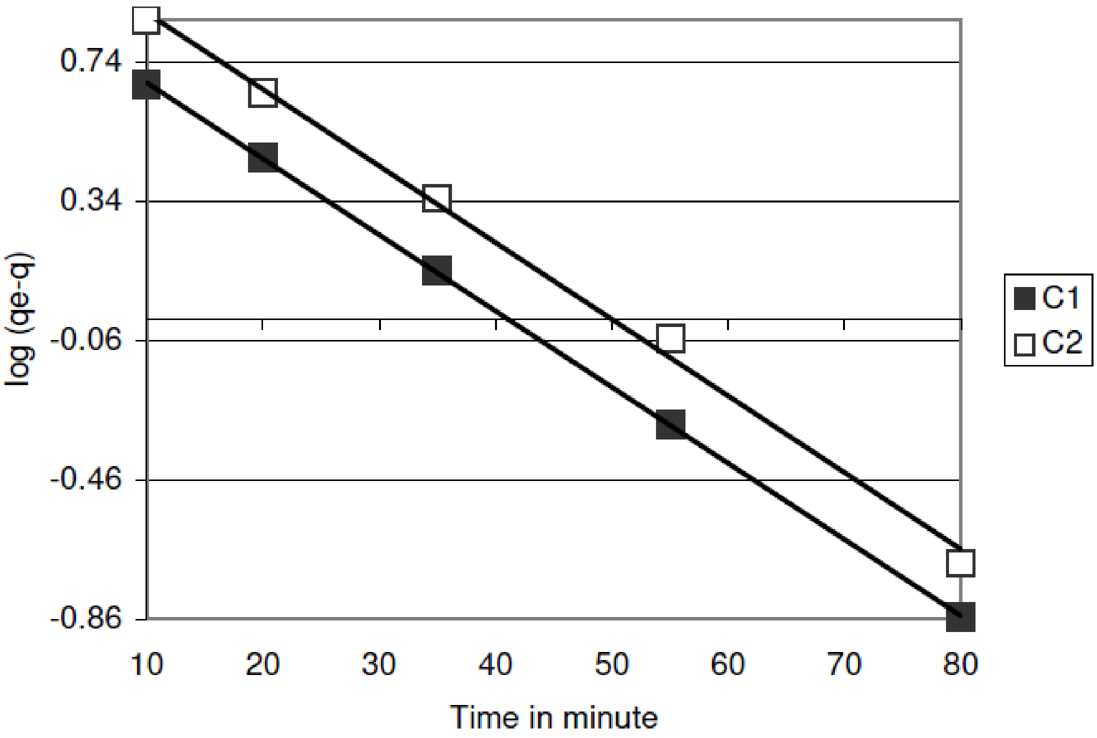


Figure 8. Lagergren Plots for methyl red adsorption on raw (C1) and pure (C2) kaolin.

very much comparable to the ones obtained in the present work.

These experiments are also comparable with the results of other investigators[Sandhya,B., Tonni,A.K., 2004,Ru-Ling Tseng, Feng-Chin Wu, Ruey-Shin Juang,2003,V.K.Garg, R.Kumar,R.Gupta,2004, V.K.Garg, R.Gupta,A.B.Bala Yadav,R. Kumar,2003,M.Do gan,M.Alkan,2003, Gurusamy Annadurai, Ruey-Shin Juang , Duu-Jong Lee 2002, Mehmet D, Gani, Mahir A and Yavuz O, 2000,Ming-Shen Chiou,Pang-Yen Ho,Hsing-Ya Li,2004, Yuh-Shan Ho, Chun-Chiao Chiang, and Yung-Chien Hsu3 2001].

4. Conclusion

Kaolin could be effectively used in scavenging colour generated by the synthetic dyes like methyl red in water. All the six kaolin samples could remove methyl red to different extents, the best results being obtained with the pure kaolin. The adsorption is favoured by acidic medium particularly between pH 3.0 and 4.0. Thus adsorption is favoured by a pH, which is below the pK_a value (≈5.05) of methyl red. Thermal treatment of kaolin was found to have negative influence on adsorption, possibly due to removal of some active sites.

Treating kaolin with NaOH modified the adsorption capacity particularly of the raw kaolin. Good fits with Freundlich and Langmuir isotherms and the values of the thermodynamic parameters show that adsorption of methyl red on kaolin is a spontaneous and favourable process. The thermodynamic parameters have values in a narrow range indicating near uniformity in the processes involved in attaining the adsorption equilibria.

No work relating to removal of methyl red from aqueous medium by adsorption has come to notice. Several reports have appeared on biological degradation of methyl red and other azo dyes. Such biodegradation has been commonly brought about by anaerobic bacteria (Roxon et al. 1967, Larsen et al. 1976, Chung et al. 1978, Zimmermann et al. 1984, Rafii et al. 1990, 1993) as well as by aerobic bacteria (Idaka et al. 1982, So et al. 1990, Yatome et al. 1990, Paszczynski et al. 1992, Govindaswami et al. 1993, Wong and Yuen 1996, Emtiazi 2000). All these works show the importance of removing methyl red either by biodegradation or by some other means from water.

In case of another acidic dye, Congo Red, Deo and Ali (1993) have reported that the adsorption of the dye on a low cost adsorbent, made from paddy straw, is not dependent on pH of the solution, but depends on the initial concentration of the dye. The present work, shows that methyl red adsorption on kaolin is dependent on pH as well as on initial concentration of the dye solution.

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