Thermodynamics and Kinetics of Adsorption of Dyes from Aqueous Media onto Alumina

[1]MUHAMMAD JAVED IQBAL AND [2]MUHAMMAD NAEEM ASHIQ*
[1]*Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan.*
[2]*Department of Chemistry, Bahauddin Zakariya Univesity, Multan-60800, Pakistan.*

(Received on 28th October 2009, accepted in revised form 26th March 2010)

Summary: Use of alumina for the removal of industrially important dyes namely, methylene blue, methyl blue, bromophenol blue, malachite green, eriochrome black-T, phenol red and methyl violet from aqueous media at different shaking times, temperatures and pH values has been investigated. The adsorption data was fitted to both the pseudo-first-order and pseudo-second-order kinetic models and calculated values of amount adsorbed at equilibrium (q_e) by pseudo-second-order equations were found to be in good agreement with the experimental values. The negative values of ΔH and ΔG indicates that the adsorption is exothermic and spontaneous, respectively. The adsorption data was fitted to Freundlich, B.E.T., Dubinin-Radushevich (D-R) and Langmuir isotherms and their corresponding adsorption parameters for each were calculated. The dyes were found to be chemisorbed onto alumina.

Introduction

Removal of hazardous industrial effluents is one of the growing needs of the present time. Most of the dyes are known carcinogens and are found to be resistant to the environmental conditions such as light and microbial attacks [1, 2]. Bromophenol blue, malachite green, phenol red and methyl violet are triphenyl methane derivative and are widely used as industrial dyes for food, drugs, cosmetics, textile, printing inks and laboratory indicator [3]. These dyes may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effect on humans. However, it is important to remove coloring materials from the effluent to save the life of both organisms which live in water and those who benefit from that water before their discharge in the environment.

Various techniques have been used for the removal of coloring materials from the waste water such as biological oxidation and electrocoagulation [4, 5]. Among these, adsorption is the most potential tool due to its high efficiency and low cost. Different adsorbents have been used for the removal of dyes from aqueous solutions [6-18]. The importance of alumina as a support, a catalyst or an adsorbent is widely recognized and is extensively employed to remove toxic and health hazardous materials [19].

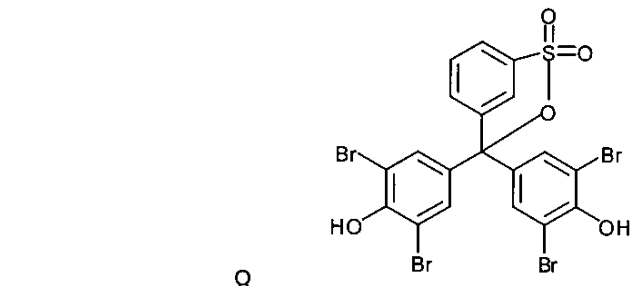
This paper presents the thermo-dynamics and kinetics parameters such as free energy changes (ΔG), enthalpy changes (ΔH), entropy changes (ΔS), pseudo-first- order rate constant (k_1), pseudo-second-order rate constant (k_2) and equilibrium concentration (q_e) for the adsorption of methyl blue, methylene blue, bromophenol blue, malachite green, methyl violet, phenol red and eriochrome black-T from aqueous solutions on alumina. The effect of temperature, pH, adsorbent dosage and contact time on the adsorption of the above mentioned dyes was also studied. Adsorption data was fitted to Freundlich, Langmuir, Dubinin-Radushevich (D-R) and B.E.T. isotherms and their corresponding adsorption parameters such as K_F, n, K, V_m, q, β and mean free energy of adsorption (E) have been calculated. The structures of the dyes are shown in (Fig. 1).

Results and discussion

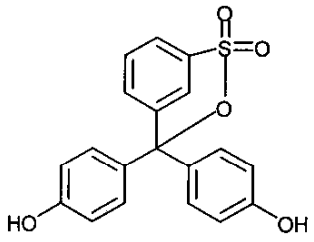
Effect of Contact Time

The contact time between the dyes and the adsorbent is of significant importance in the waste water treatment by adsorption methods. A rapid removal of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in the waste water treatment. The effect of shaking time for the adsorption of dye solutions was determined at 298 K. Experiments were performed using a 25 mL aqueous solutions of fixed concentration for each dye and were shaken together with 0.2 or 0.3 g of alumina, as

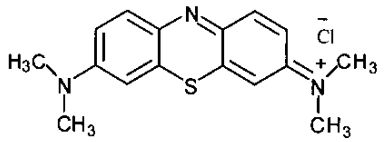
*To whom all correspondence should be addressed.



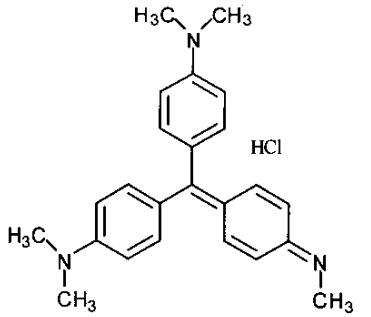
Bromophenol Blue (3.42 nm^2)



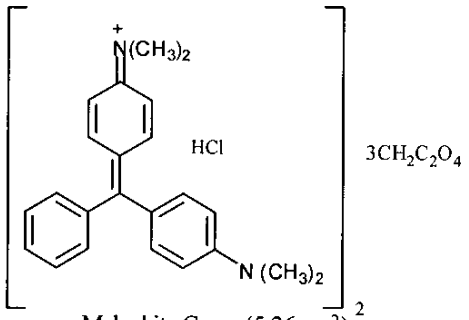
Phenol Red (2.49 nm^2)



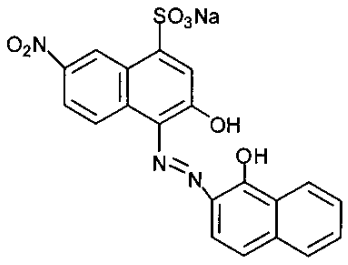
Methylene Blue (2.70 nm^2)



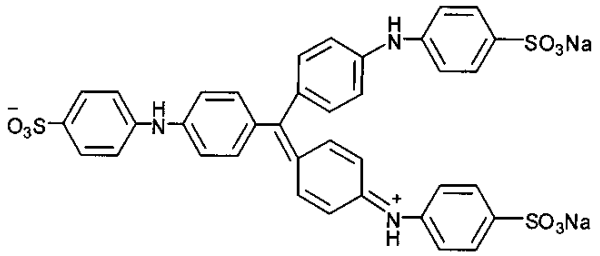
Methyl Violet (3.51 nm^2)



Malachite Green (5.26 nm^2)



Eriochrome Black T (3.48 nm^2)



Methyl Blue (5.81 nm^2)

Fig. 1: Structures of dyes.

the case may be, for different intervals of time ranging from 5 to 60 minutes. It is clear from Fig. 2 that the color removal is initially rapid due to the presence of a large number of vacant surface sites but it slows down to almost a constant value at a later stage. The steric hindrance of the bulkier adsorbed dye molecules for those in the bulk may be one of the causes of this decline. An optimum shaking time of

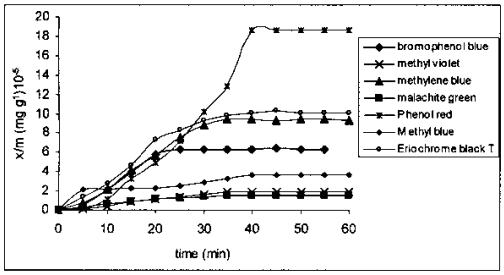


Fig. 2: Effect of shaking time on the adsorption capacity of alumina for various dyes.

40 minutes was determined and therefore the samples were shaken for this period of time in every experiment.

Effect of Amount of Adsorbent

For the purpose of optimizing the amount of the adsorbent, experiments were performed using a 25 mL aqueous solutions of bromophenol blue, phenol red, and methylene blue, malachite green, eriochrome black T, methyl blue and methyl violet (2×10^{-5} mol L^{-1}) and were shaken together for 40 minutes adding different amount of alumina. The absorbance of the filtrate was noted by the spectrophotometer at the λ_{max} of each dye. (Fig. 3) shows that adsorption of dyes increased with increasing the amount of alumina and then attain constant value when equilibrium was established. The optimum amount was found to be 0.2 g for bromophenol blue, malachite green, methylene blue, methyl blue and methyl violet and (0.3 g) for phenol red and eriochrome black T, which was used for all further adsorption studies.

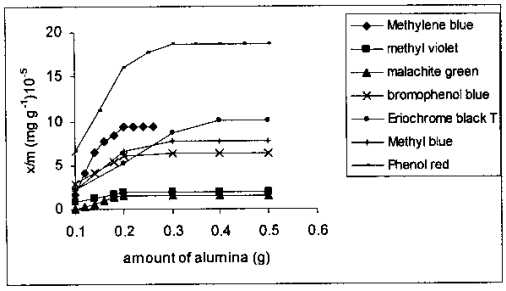


Fig. 3: Effect of amount of adsorbent on the adsorption process at 298K.

Adsorption Isotherms

Although the adsorption isotherms of the various dyes were obtained at several temperatures *i.e.* 298, 303, 308, 313, and 318 K but only the isotherms at 298 K have been presented here (Fig. 4). The initial sharp rise in the extent of adsorption with increasing dye concentration is due to higher adsorption potential of the surface at the beginning whereas the bombarding solute molecules find it difficult to access the remaining vacant surface sites due to decrease in the adsorption potential of alumina surface with more and more sites being filled up.

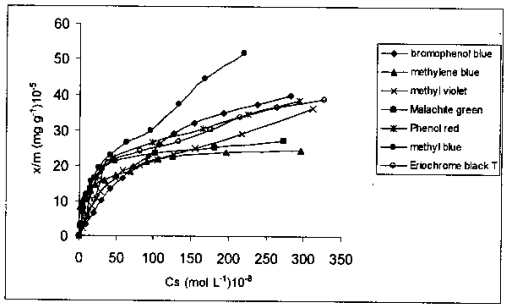


Fig. 4: Adsorption isotherms of various dyes on alumina at 298 K.

The extent of adsorption of all the dyes investigated in the present study is found to be decreased with the increase in temperature however, only one representative graph has been shown in (Fig. 5). This indicates that desorption process is more favorable at higher temperature than the adsorption process in accordance with Le Chatelier's principle and is expected of an exothermic process.

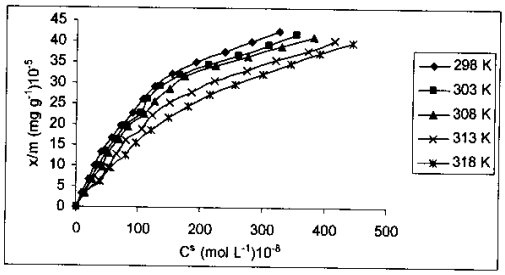


Fig. 5: Adsorption isotherms of bromophenol blue on alumina at various temperatures.

The molecular size of the dye molecule is an important parameter in the adsorption process. The Connolly molecular surface areas of the dye molecules were determined using the software package CS Chem 3D Ultra [20] and are given in (Fig. 1). The expected order of adsorption capacity on the basis of molecular sizes of the dyes should be phenol red > methylene blue > bromophenol blue > eriochrome black-T > methyl violet > malachite green > methyl blue. Unfortunately, Fig. 4 shows the order of adsorption capacity in the order as, methyl blue > bromophenol blue > phenol red > eriochrome black-T > methyl violet > malachite green > methylene blue. This may be due to steric hindrance and multiple interactions.

The Freundlich plots for each dye are shown in (Fig. 6) and values of the Freundlich constants, K_F and n, are given in Table-1. If n = 1, the adsorption is homogeneous and there is no interaction between the adsorbed species. If n < 1, the adsorption is unfavorable and if n > 1, then the adsorption is favored and new sites are generated. In present studies, we have found for all the dyes n is greater than unity which indicates that the adsorption is favorable. It may be noted that the values of K_F and n decrease with an increase in temperature indicating that adsorption may be favorable at low temperatures. The value of n is greater than unity in all the cases which indicates the amount adsorbed increases less rapidly than the concentration of the dyes.

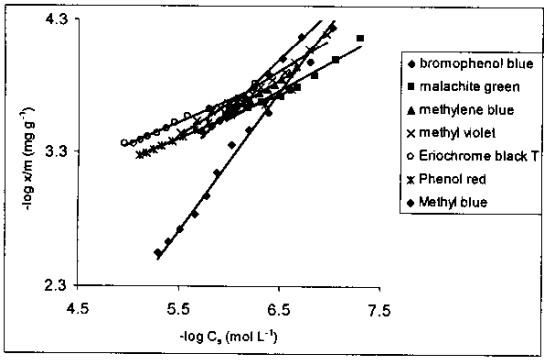


Fig. 6: Freundlich isotherms of various dyes on alumina at 298 K.

Langmuir isotherm is found to be obeyed by all the dyes as shown in (Fig. 7). This indicates that the dyes are chemisorbed on the surface of the alumina. The values of the adsorption coefficient K

Table-1: Freundlich Parameters for various dyes on activated Alumina.

Dyes	Temp.(K)	n	K_F	R^2
Bromophenol Blue	298	1.3665	5.721	0.991
	303	1.3514	5.577	0.983
	308	1.3417	5.563	0.976
	313	1.3275	5.354	0.994
	318	1.3158	5.245	0.989
Erichrome Black T	298	1.3396	2.964	0.980
	303	1.3457	2.688	0.975
	308	1.3604	2.257	0.983
	313	1.3515	2.196	0.968
	318	1.3535	1.953	0.980
Malachite Green	298	1.5482	3.160	0.960
	303	1.5359	2.842	0.951
	308	1.5168	2.613	0.970
	313	1.5078	2.316	0.962
	318	1.5015	2.355	0.986
Methylene Blue	298	1.4267	5.213	0.982
	303	1.4963	3.006	0.987
	308	1.4817	2.807	0.990
	313	1.5078	2.239	0.971
	318	1.5081	2.074	0.984
Methyl Blue	298	1.5820	192.13	0.988
	303	1.5659	180.92	0.995
	308	1.5610	171.71	0.980
	313	1.5513	168.81	0.988
	318	1.5640	149.59	0.990
Methyl Violet	298	1.5172	2.136	0.977
	303	1.5040	2.067	0.948
	308	1.4937	2.025	0.953
	313	1.4854	2.013	0.906
	318	1.4658	1.982	0.948
Phenol Red	298	1.4899	1.775	0.994
	303	1.4760	1.705	0.986
	308	1.4693	1.610	0.973
	313	1.4939	1.283	0.990
	318	1.4749	1.247	0.993

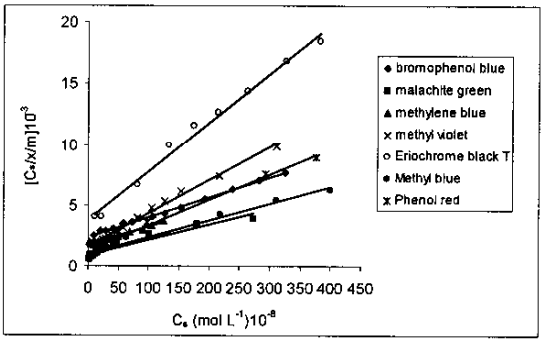


Fig. 7: Langmuir isotherms of various dyes on alumina at 298 K.

and the monolayer capacity V_m calculated from Langmuir plots are given in Table-2. The values of K and V_m are found to decrease with increasing temperature. It was found that the adsorption data provides a good fit of the Langmuir isotherm. The B.E.T equation is not obeyed by any of the dyes suggesting that the dyes are not physically adsorbed on alumina surface as shown in (Fig. 8).

Table-2: Langmuir parameters for various dyes on activated Alumina.

Dyes	Temp./K	K (10^5)/ dm^3mg^{-1}	V_m (10^{-3})/mgg^{-1}	R^2
Bromophenol	298	6.3597	62.897	0.996
Blue	303	5.6954	62.708	0.993
	308	5.6351	61.192	0.989
	313	4.5629	60.879	0.990
	318	2.9188	69.920	0.986
Eriochrome	298	2.3694	62.992	0.990
Black-T	303	2.3967	60.470	0.982
	308	2.2477	58.538	0.993
	313	2.3648	54.212	0.994
	318	2.0476	52.513	0.989
Malachite	298	54.891	30.363	0.940
Green	303	39.615	31.554	0.953
	308	33.034	30.721	0.957
	313	21.985	30.323	0.961
	318	22.414	29.743	0.968
Methylene	298	12.462	53.496	0.983
Blue	303	12.541	49.836	0.990
	308	10.588	47.223	0.993
	313	10.110	44.960	0.986
	318	9.450	44.098	0.979
Methyl	298	5.616	89.000	0.981
Blue	303	3.376	98.750	0.986
	308	3.229	103.200	0.972
	313	3.235	103.100	0.980
	318	2.346	106.600	0.989
Methyl	298	22.237	32.121	0.993
Violet	303	16.833	33.004	0.990
	308-	15.365	32.543	0.996
	313	13.230	32.862	0.991
	318	11.233	31.794	0.993
Phenol	298	4.103	69.628	0.992
Red	303	3.267	69.575	0.983
	308	2.678	70.452	0.990
	313	2.718	62.367	0.996
	318	2.519	58.384	0.987

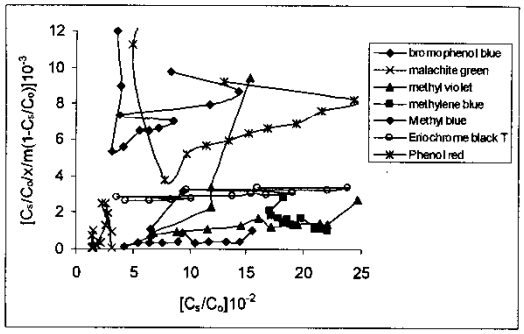


Fig. 8: BET isotherms of various dyes on alumina at 298 K.

The values of the regression parameters and the correlation coefficient (R^2) of the plot $\ln(x/m)_e$ versus ε^2 (Fig. 9) are presented in Table-3. The values of correlation coefficient vary from 0.957-0.996, suggests that this isotherm obeyed by the experimental data. The values of q decrease with the temperature suggesting that the adsorption capacity

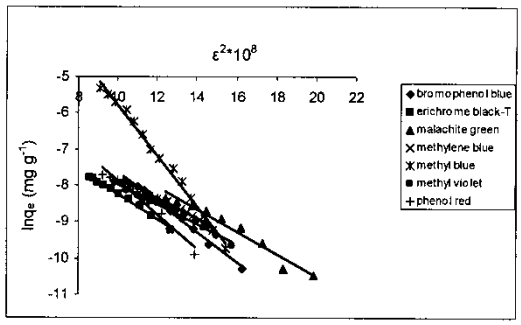


Fig. 9: D-R isotherms for the adsorption of various dyes onto alumina at 298 K.

Table-3: Dubinin-Radushkevich parameters for various dyes on activated Alumina.

dyes	Temp./ K	q/ mg g^{-1}	β/ mol^2kJ^{-2} (10^{-9})	E/ $kJmol^{-1}$	R^2
Bromophenol blue	298	0.0290	4.11	11.03	0.992
	303	0.0291	4.10	11.04	0.989
	308	0.0287	4.09	11.06	0.982
	313	0.0282	4.07	11.08	0.990
	318	0.0280	4.09	11.06	0.986
Eriochrome Black-T	298	0.0078	3.40	12.13	0.994
	303	0.0073	3.40	12.13	0.995
	308	0.0071	3.41	12.11	0.991
	313	0.0072	3.39	12.14	0.994
	318	0.0069	3.39	12.14	0.990
Malachite green	298	0.0133	3.10	12.70	0.963
	303	0.0136	3.12	12.66	0.957
	308	0.0135	3.11	12.68	0.960
	313	0.0132	3.08	12.74	0.967
	318	0.0131	3.06	12.78	0.951
Methylene blue	298	0.0067	2.83	13.29	0.981
	303	0.0064	2.81	13.34	0.985
	308	0.0062	2.80	13.36	0.986
	313	0.0063	2.83	13.29	0.981
	318	0.0060	2.82	13.32	0.978
Methyl blue	298	3.254	6.92	8.50	0.991
	303	3.247	6.91	8.51	0.993
	308	3.236	6.87	8.53	0.984
	313	2.238	6.86	8.54	0.996
	318	2.229	6.84	8.55	0.991
Methyl violet	298	0.0053	2.74	13.51	0.986
	303	0.0051	2.71	13.58	0.990
	308	0.0052	2.70	13.61	0.992
	313	0.0048	2.72	13.56	0.986
	318	0.0041	2.69	13.63	0.979
Phenol Red	298	0.0432	4.72	10.29	0.964
	303	0.0433	4.70	10.31	0.972
	308	0.0430	4.66	10.36	0.976
	313	0.0425	4.68	10.34	0.963
	318	0.0422	4.67	10.35	0.957

of the adsorbent decreases as the temperature increases. The mean adsorption energy (E) calculated from eq. 7 provides important information about these properties [21]. For E < 8 kJ mol^{-1}, physisorption dominates the adsorption mechanism.

If E is between 8 and 16 kJ mol^{-1}, adsorption is dominated by ion-exchange indicating that chemisorption occurs in the adsorption process [21]. The values of E are shown in Table-3 and are in between 8 and 16 kJ mol^{-1}, suggesting the chemisorption of these dyes. The BET isotherm also confirms the chemisorption of these dyes onto the surface of alumina.

Effect of pH

Since the hydrogen and hydroxyl ions are usually adsorbed quite strongly on the surface therefore the adsorption of other ions is affected by the pH of the solution [22]. The pH primarily affects the degree of ionization of the dyes as well as the surface properties of the adsorbents. It has been reported that anions are more favorably adsorbed at lower pH values than cations whose adsorption is preferable at higher pH due to deposition of OH^- ions on the surface [23]. Fig. 10 shows that the adsorption of the bromophenol blue, eriochrome black T, phenol red and methyl blue decreased with pH whereas for methylene blue, methyl violet and malachite green the adsorption increased on alumina. This can be explained on the basis that positively charged surface is formed on alumina at lower pH. In the aqueous solution the methyl blue and eriochrome black-T first dissolve and then the sulfonate group of these dyes are dissociated and converted to anionic dyes ions as follows; eq 1.

$$A\text{-}SO_3H \xrightarrow{H_2O} A\text{-}SO_3^- + H^+ \quad (1)$$

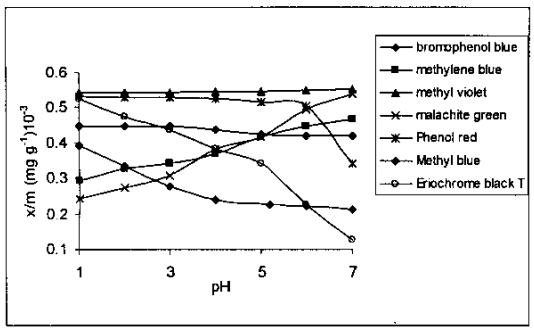


Fig. 10: Effect of pH on the adsorption capacity of alumina for various dyes at 298 K.

where "A" stands for methyl blue and eriochrome black-T. As the pH of the system is increased the number of positively charged site on the surface of alumina decreased and the adsorption of these dyes decreased because these dyes dissociate and have a negative charge. The bromophenol blue and phenol red are also anionic dyes and their adsorption also decreased with the increase in pH of the system. The adsorption of malachite green, methylene blue and methyl violet increased with increasing the pH of the solution. These dyes get protonated in the acidic medium and deprotonated at higher pH. Consequently, the dyes molecules have high positive charge density at lower pH. Therefore, for pH below 7, the electrostatic repulsion between the positively charged surface of the alumina and the positive charged dye molecules may be present. Also, the lower adsorption of these dyes in acidic pH is due to the presence of excess hydrogen ions competing with dye cations for the adsorption. The increase in adsorption with pH for these dyes was also observed by several researchers [23-25]. In the present study, the effect of pH on adsorption of dyes within pH range 1-7 could only be studied because the λ_{max} of the dyes change above pH 7.

Adsorption Kinetics

In order to investigate the adsorption processes of the various dyes on alumina two kinetic models were used. Fig. 11 shows the plots for the pseudo-first-order model and the values of k_1 and q_e are tabulated in Table-4. The plot has correlation coefficient 0.845-0.973 but the values of q_e are dramatically different from the experimental values. It has been reported that if the values of q_e are not the same as the experimental value, the kinetic of adsorption is not followed by this model even it has high correlation coefficient [26]. So the second model was tested.

Fig. 12 shows the plot of t/q_t versus t and the values of q_e and k_2 were obtained from the slope and intercept, respectively are shown in Table-4. The values of q_e are very close to the experimental values. Therefore, the adsorption of selected dyes on alumina is more appropriately followed by the pseudo-second-order kinetic model even it has smaller correlation coefficient for some dyes than the pseudo-first-order kinetic model.

Thermodynamic Studies

The negative values of free energy ΔG (Table-5) indicate the feasibility of the process and

Table-4: Kinetics parameters for the adsorption of various dyes on activated alumina.

Dyes	qe (Exp.)/ mg g^{-1} (10^{-5})	Pseudo-first order q_e/mgg^{-1}	k_1/min^{-1}	R^2	Pseudo-second order q_e/mgg^{-1} (10^{-5})	k_2/g mg^{-1} min^{-1} (10^3)	R^2
Bromophenol blue	6.20	0.029	0.085	0.898	6.34	31.99	0.996
Erichrome Black- T	9.08	0.024	0.041	0.954	9.53	1.97	0.766
Malachite green	1.46	0.010	0.045	0.954	1.40	22.44	0.996
Methylene blue	10.98	0.025	0.045	0.891	11.34	0.75	0.711
Methyl blue	1.97	0.007	0.008	0.845	2.50	53.07	0.993
Methyl violet	2.14	0.011	0.033	0.973	2.01	5.49	0.716
Phenol Red	22.61	0.030	0.031	0.923	21.53	0.19	0.383

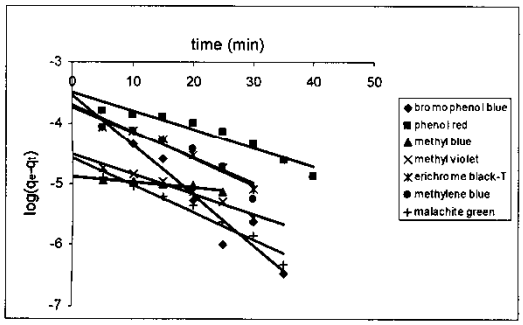


Fig. 11: Pseudo-first-order kinetics plot for the adsorption of various dyes on alumina at 298 K.

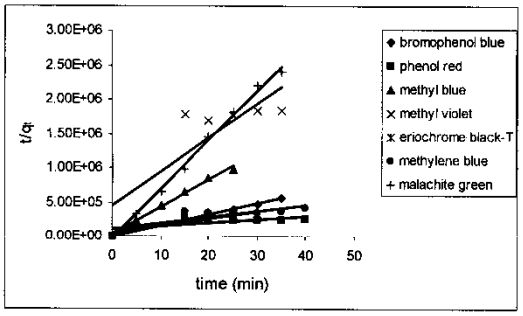


Fig. 12: Pseudo-second-order kinetics plot for the adsorption of various dyes on alumina at 298 K.

its spontaneous nature. The ΔG values at different temperatures approximately remain constant for the specific dye indicating that there is no effect of temperature on free energy of adsorption.

The ΔH and ΔS were calculated from the plot of InK versus 1/T as shown in Fig. 13 and their values are shown in Table-5. The negative values of ΔH for all the systems confirm the exothermic nature of adsorption. It has been reported that the enthalpy change of adsorption of methylene blue on fullers

Table-5: Thermodynamic parameters for the adsorption of various dyes on activated Alumina.

Dyes	Temp. /K	-ΔG/KJ mol^{-1}	-ΔH/ KJ mol^{-1}	+ΔS/ KJ mol^{-1}K^{-1}
Bromophenol Blue	298	33.108	26.750	0.0219
	303	33.386	"	"
	308	33.909	"	"
	313	33.910	"	"
	318	33.270	"	"
Erichrome Black T	298	30.662	18.796	0.0432
	303	31.205	"	"
	308	31.556	"	"
	313	32.201	"	"
	318	32.333	"	"
Malachite Green	298	38.447	36.178	0.0071
	303	38.271	"	"
	308	38.436	"	"
	313	38.001	"	"
	318	38.661	"	"
Methylene Blue	298	34.775	11.555	0.0781
	303	35.374	"	"
	308	35.525	"	"
	313	35.979	"	"
	318	36.377	"	"
Methyl Blue	298	32.801	27.107	0.0179
	303	32.069	"	"
	308	32.483	"	"
	313	33.015	"	"
	318	32.694	"	"
Methyl Violet	298	36.210	24.348	0.0393
	303	36.114	"	"
	308	36.447	"	"
	313	36.679	"	"
	318	36.834	"	"
Phenol Red	298	32.023	17.543	0.0479
	303	31.986	"	"
	308	32.004	"	"
	313	32.562	"	"
	318	32.882	"	"

earth [27], wheat shells [28], activated carbon prepared by waste apricot [15] has a positive value but have negative values on red mud [27]. The malachite green showed endothermic nature on activated carbon obtained from waste apricot [15] and waste slurry [28] but exothermic nature on 'neem' saw dust [29]. The eriochrome black-T and bromophenol blue have positive and negative values of ΔH by adsorption on mesoporous hybrid gel [3], respectively. The negative values of ΔG for these dyes reported in the present study are in good agreement with literature [3, 22, 28, 29]. The

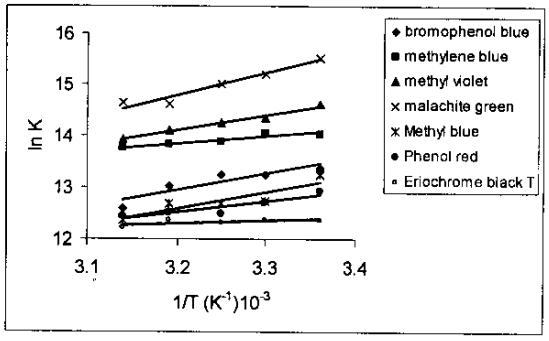


Fig. 13: Plots of lnK *vs* 1/T for the adsorption of various dyes on alumina.

adsorption data fit better to the Langmuir and D-R isotherms (Figs. 7 and 9) but poor fit to the BET isotherm (Fig. 8) although the values of ΔH are less than 40 kJmol^{-1}. Additionally, the values of the mean adsorption energy, E (8-13K J mol^{-1}) shown in Table-3 also indicate chemisorptions.

The positive value of ΔS observed for the adsorption of dye molecules suggested the increased randomness at the solid-solution interface during the adsorption process. The dye molecules in the aqueous media are hydrated. When the dye molecules get adsorbed on the adsorbent surface, the water molecules previously hydrogen bonded to the dye molecules get released and dispersed in the solution, this results in an increased in the entropy. The positive values of entropy change also reflect good affinity of the dyes toward the adsorbent. The entropy changes results in the present studies are in excellent agreement with the literature [27, 28].

Materials and Methods

Bromophenol blue (95%, Perking Chemical, China), methylene blue (82%, Fluka), methyl blue (60%, Fluka), methyl violet (85%, Fluka), phenol red (95%, Polskie Odezynniki), eriochrome black T (65%, Riedel-de Haen), malachite green oxalate (90%, Merck) and the adsorbent alumina type-E supplied by Merck were used without further purification. The structures of the dyes are shown in (Fig. 1).

Adsorption Studies

Stock solutions of dyes (1×10^{-3} mol L^{-1}) were initially prepared by dissolving weighed amounts of each dye in distilled water and thereby necessary dilutions were made in the same solvent. The absorbance of the dye solutions was measured at various wavelengths and values of λ_{max} were found to be 435, 530, 585, 590, 610, 620 and 665 nm for phenol red, eriochrome black-T, methyl violet, bromophenol blue, methyl blue, malachite green and methylene blue, respectively. The blank experiments were performed in order to investigate the adsorption of each dye on the filter paper during filtration and it was observed that a minute quantity (less than 3%) of the dye was removed by the filter paper during filtration and therefore the final values were corrected accordingly. Optimized amounts of alumina, 0.2 g for bromophenol blue, malachite green, methylene blue, methyl blue and methyl violet and, 0.3 g for phenol red and eriochrome black-T were taken in a flask containing 25 mL dye solution and was shaken in a water bath incubator (Hitachi BT-47) at the rate of 120 strokes/min at 298, 303, 308, 313 and 318 K. The solutions were filtered. The dye concentration in the aqueous phase was recorded by a spectrophotometer (Shimadzu UV-120-01) at their respective λ_{max} of each dye. The amount adsorbed, x/m (mg g^{-1}) was plotted against the equilibrium concentration, C_s (mol L^{-1}) and the adsorption isotherms were constructed.

Buffer solutions of various pH ranging 1-7 were used; buffers of pH 1, 2, 4, and 7 were supplied by Fluka and of pH 3, 5, and 6 was prepared [19]. Buffer of pH 5 from the mixture of 0.1 mol dm^{-3} potassium hydrogen phthalate and NaOH. Buffer of pH 3 was prepared from the mixture of 0.1 mol dm^{-3} of potassium hydrogen phthalate and HCl. Buffer of pH 6 was prepared from the mixture of 0.1 mol dm^{-3} of potassium dihydrogen phosphate and NaOH. The various dye solutions were prepared by taking 2 mL of dye stock solution (1×10^{-3} M) and their volumes were made up to 100mL with buffer solutions of respective pH. The solution pH was monitored by a pH meter (Model HM-7E). Optimum amount of alumina *i.e.* 0.2 or 0.3 g (as mentioned above) in a flask containing 25 mL dye solutions of various pH were shaken in a water bath incubator at a rate of 120 strokes/min at 298 K. The solutions were filtered and less than 3% dyes were deposited on the filter paper and was deducted from the final results accordingly. The concentrations of the unadsorbed dyes were determined by a spectrophotometer at their respective λ_{max}. The amount adsorbed, x/m (mg g^{-1}) is plotted against pH.

Calculations

Adsorption data for the dyes on alumina was fitted to the linear form of Freundlich (Eq. 2), Langmuir (Eq. 3), BET isotherms (Eq. 4) and D-R (Eq. 6) as shown in Figures (6, 7, 8 and 9) [30].

$$\log x/m = \log K_F + 1/n \log C_s \qquad (2)$$

where x/m is the amount adsorbed per unit mass of the adsorbate, C_s is the equilibrium concentration; K_F and 1/n are constants, being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and the adsorption, respectively. The values of K_F and n were determined from intercepts and slopes of the linear plots of log C_s versus log x/m, respectively.

Langmuir equation is given as

$$\frac{C_s}{x/m} = \frac{1}{KV_m} + \frac{C_s}{V_m} \qquad (3)$$

where K is the adsorption coefficient and V_m is the monolayer capacity and their values were calculated from the plot of C_s against C_s/x/m.

The B. E. T. equation is as follows

$$\frac{C_s/C_0}{x/m\left(1-C_s/C_0\right)} = \frac{1}{x_m C} + \frac{C-1}{x_m C}\cdot C_s/C_0 \qquad (4)$$

where "x_m" is the monolayer capacity and "C" is a constant.

The Dubinin-Radushevich (D-R) isotherm [31], which assumes a heterogeneous surface, is expressed as follows:

$$(x/m)_e = q \exp(-\beta\varepsilon^2) \qquad (5)$$

where $(x/m)_e$ is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), q is the adsorption capacity of the adsorbent (mg g^{-1}), β is a constant related to the mean adsorption energy (mol^2 kJ^{-2}) and ε is the Polanyi potential and is given as

$$\varepsilon = RT(1+1/C_e) \qquad (6)$$

where R is gas constant (kJ K^{-1} mol^{-1}), T is the temperature (K) and C_e is the equilibrium concentration of the dyes in solution (mol L^{-1}).

The D-R isotherm can be expressed in linear form as follows

$$\ln(x/m)_e = \ln q - \beta\varepsilon^2 \qquad (7)$$

The values of adsorption capacity of the adsorbent (q) and β were calculated from the graphs of ε^2 against $\ln(x/m)_e$. The mean adsorption energy (E, kJ mol^{-1}) can be obtained from β values of the D-R isotherm [31] using the following equation

$$E = \frac{1}{(2\beta)^{1/2}} \qquad (8)$$

The pseudo-first-order equation is given as [21]

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \qquad (9)$$

where q_t is the amount of dyes adsorbed at time t (mg g^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1}), k_1 the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min). The integration of eq. 8 with initial conditions, $q_t = 0$ at $t = 0$ leads to

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (10)$$

The values of the constants, k_1 and q_e for the adsorption of dyes on alumina were determined from the slopes and intercepts of the plots $\log(q_e-q_t)$ against.

The pseudo-second-order model can be represented in the following form [21]

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad (11)$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). Integrating eq. 10 and noting that $q_t = 0$ at $t = 0$, the equation obtained is

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t \qquad (12)$$

The values of the q_e and k_2 were determined by plotting a graph between t/qt and time.

The free energy of the adsorption was calculated by following equation

$$\Delta G = -RT \ln K \qquad (13)$$

where "K" is the adsorption coefficient obtained from the Langmuir equation. The changes in the enthalpy and entropy of adsorption were calculated from the slopes and intercepts of the plots lnK versus reciprocal of temperature, respectively, in accordance with the following equation

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (14)$$

Conclusion

The present investigation shows that alumina can be utilized for the removal of hazardous dyes from the aqueous solutions. The adsorption process is a function of shaking time, pH and temperature. It was observed that the adsorption process followed the pseudo-second-order kinetics model. The values of q_e calculated from pseudo-second-order plots are in good agreement with the experimental values. Thermodynamic study showed that the process is spontaneous and exothermic. The entropy of adsorption was found to be positive for the dyes which reflect good affinity of dyes toward adsorbent. The adsorption isotherms for the dyes investigated here are of L-type. The adsorption data showed a batter fit in accordance with the Langmuir isotherm and not by B. E. T. isotherm suggesting chemisorption of the dyes onto alumina. The values of "E" also confirm the chemisorption of these dyes.

References

1. G. Baughman, and T. A. Perenich, *Toxicological and Environmental Chemistry,* **18**, 183 (1998).
2. U. M. Pagga, and K. Taeger, *Water Research,* **28**, 1051 (1994).
3. L. You, Z. Wu, T. Kim, and K. Lee, *Journal of Colloid and Interface Science,* **300**, 526 (2006).
4. A. K. Golder, A. N. Samanta, and S. Ray, *Chemical Engineering Journal,* **122**, 107 (2006).
5. S. M. Ghoreishi, and R. Haghighi, *Chemical Engineering Journal,* **95**, 163 (2003).
6. O. Hamdaou, *Journal of Hazardous Materials,* **135**, 264 (2006).
7. Y. S. Ho, and G. Mckay, *Chemical Engineering Journal,* **70**, 115 (1998).
8. S. B. Bukallah, M. A. Rauf, and S. S. Ali, *Dyes and Pigments,* **74**, 85 (2007).
9. E. Eren, and B. Afsin, *Dyes and Pigments,* **74**, 220 (2008).
10. C. Gregorio, *Dyes and Pigments,* 77, 415 (2008).
11. H. L. Chiang, K. H. Lin, S. Y. Chen, C. G. Choa, and S. D. Pan, *Dyes and Pigments,* **75**, 52 (2007).
12. M. A. Rauf, M. J. Iqbal, M. Ikram, and N. Rauf, *Journal of Trace and Microprobe Techniques,* **21**, 337 (2003).
13. A. J. Agnieszka, K. Andrzej, and J. Teofil, *Dyes and Pigments,* **75**, 116 (2007).
14. A. Mahir, C. Sermet, D. Ozkan, and D. Mehmet, *Dyes and Pigments,* **65**, 251 (2005).
15. Y. Onal, *Journal of Hazardous Materials,* **137**, 1719 (2006).
16. A. Adak, M. Bandyopadhyay, and A. Pal, *Separation and Purification Technology,* **44**, 139 (2005).
17. A. S. Gawade, A. K. Vanjara, and M. R. Sawant, *Separation and Purification Technology,* **41**, 65 (2005).
18. M. Afzal, M. Khan, and H. Ahmad, *Colloid and Polymer Science,* **269**, 483 (1991).
19. D. R. Lide, R. CRC Hand book of Chemistry and Physics, 86th ed., p 8-39, 2005-2006.
20. Y. C. Wong, Y. S. Szeto, W. H. Cheung, and G. Mckay, *Langmuir,* **19**, 7888 (2003).
21. M. E. Argun, S. Dursun, C. Ozdemir, and M. Karatas, *Journal of Hazardous Materials,* **141**, 77 (2007).
22. M. J. Iqbal, and M. Hussain, *Journal of the Chemical Society of Pak,* **15**, 7 (1993); **ibid,** *Journal of the Chemical Society of Pakistan,* **15**, 93 (1993).
23. I. D. Mall, V. C. Srivastava, N. K. Agarwal, and I. M. Mishra, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **264**, 17 (2005); **ibid,** *Dyes and Pigments,* **69**, 210 (2006).
24. S. Wang, Y. Boyjoo, and A. Choueib, *Chemosphere,* **60**, 1401 (2005).
25. M. J. Iqbal, and M. N. Ashiq, *Journal of Hazardous Materials,* **B139**, 57 (2007).
26. E. L. Grabowska, and G. Gryglewicz, *Dyes and Pigments,* **74**, 34 (2007).
27. A. Ramesh, D. J. Lee, and J. W. C. Wong, *Journal of Colloid and Interface Science,* **291**, 588 (2005).
28. Y. Bulut, and H. Aydin, *Desalination,* **194**, 259 (2006).
29. S. D. Khattri, and M. K. Singh, *Water, Air and Soil Pollution,* **120**, 283 (2000).
30. G. C. Bond, Heterogeneous catalysis: principles and applications, 2nd ed, Oxford University press, New York, p 16-20 (1987).
31. Z. Bekci, Y. Seki, and M. K. Yurdakoc, *Journal of Molecular Structure,* **827**, 67 (2007).