Adsorption of Acid Red in Zeolites

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Zeolites are important inorganic compounds which exhibit a very high surface activity with an internal pore system of molecular dimensions. A very important property of zeolites which is based on the molecular sieve effect, is their preferential adsorption of polar, unsaturated and aromatic compounds. Surface characterization and dehydration kinetics of zeolites have been previously investigated [1,2]. Reactive dyes in the waste water cannot be removed adequately, so an improved procedure is necessary to avoid damage to the aquatic environment. In this communication adsorption of acid red on zeolites is reported.

The zeolites were activated by heating in a furnace at 350° for 2 hrs. A series of solutions of acid red of various concentrations and definite volume was made up in the bottle and a definite amount of adsorbent was added. These bottles were shaken in a thermostated shaker at 120 strokes per minutes for 50 mm until equilibrium was attained. The contents were filtered and the first 10 ml of the filtrate was rejected. The absorption spectra was recorded by spectrophotometer. The amount of the dye adsorbed per grame of the adsorbents (X/m) were calculated from the difference in the initial and final concentration. A plot of X/m vs equilibrium concentration (Cs) represents the adsorption isotherm as shown in Figs. 1-2. The dye solution was covered with thick black cloth to protect it from the effect of light.

The adsorption force in zeolites is due primarily to the exchangeable cations exposed in the crystal adsorption surface. These cations act as sites of strong localized positive charge which electrostatically attracts the negative end of polar or polarisable molecules. The initial curvature (Figs. 1-2) shows that more sites in the substrate are filled at low concentration and at higher partial pressure it becomes difficult for bombarding solute molecules to find vacant sites available.

The adsorption of acid red on zeolites 3A and 4A follows Freundlich isotherm [2-3]. The values of constants K and 1/n were computed from the slope and intercept of a plot of log (X/m) in g/g vs equilibrium concentration Cs in moles/liter. The parameter K refer to the adsorption capacity and 1/n gives the intensity of adsorption. These values for both systems are shown in Table 1. The values of K increase with increase in temperature, indicating that adsorption is more favourable at high temperature.

The adsorption of acid red on zeolites 3A and 4A also obey Dubinin-Radushkevich Isotherm equation [4]. The values of Xm and K were computed from the linear plot of ln X vs ε^2. Xm values were computed from the intercept and slope giving the values of K. The mean free energy of sorption (E) is the free energy change where one mole of dye is transferred to the surface of the solid from infinity in solution. It is calculated as [5,6].

$$E = (-2K)^{-1/2}$$

The magnitude of E is useful for estimating the type of sorption reaction occurring. The values of E for acid red on zeolites 3A and 4A are shown in Table 2 at different
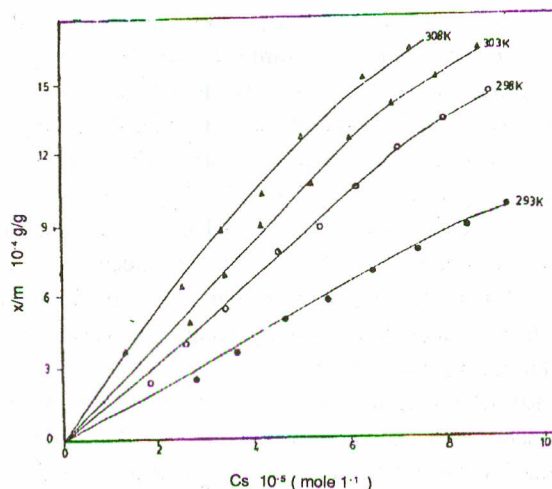

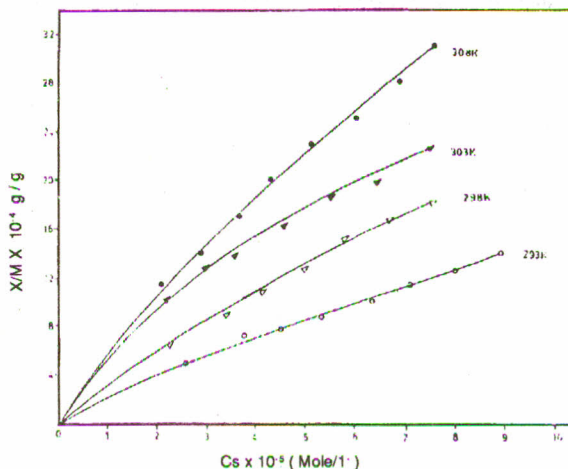Fig. 1. Adsorption isotherms of acid red on zeolite 3A at different temperatures.

Fig. 2. Adsorption isotherms of acid red on zeolite 4A at different temperatures.

temperatures. They were found to be 2-6 Kcal/mole, which is in the energy range of ion exchange reactions [7,8]. It is evident from these tables that values of E increase with rise in temperature, showing an increase in ion exchange reaction with rise in temperature.

The parameters $1/K_1k$ and $1/K$ were computed from Langmuir plots of (Cs / (X/m)) vs Cs. The slope gives the values of $1/K$ from which the monolayer capacity Vm was computed. The values of monolayer capacity increase with rise in temperature and indicates the strengthening of dye zeolite interactions at high temperature.

The heats of adsorption were calculated by the use of Langmuir constant K in the equation [9-11] as:

$$\ln K = \Delta S/R - \Delta H/RT \qquad (1)$$

where K = binding constant (1/g).

The values of ΔS and ΔH were calculated from the linear plot of ln K vs 1/T. Heats of adsorption were computed, from the slope and values of ΔS were computed from the intercept respectively. The values of standard free energy ΔG were calculated by making use of the familiar equation as:

$$\Delta G = \Delta H - T \Delta S \qquad (2)$$

The values of thermodynamic parameters are summarized in Table 3. It is evident from the data that the values of ΔH are positive showing non localized adsorption on the zeolite surface. With increase in temperature adsorption increases, indicating the endothermic nature of adsorption [12]. For those systems in which adsorption increases with rise in temperature, there is good evidence [13] that the dye molecules are highly aggregated in solution and thus the solutions do not obey the Lambert-Beer law and show marked light scattering. Thus the apparent endothermic nature of the system is therefore a result of the aggregation of the solutes in solution. Physiosorption is characterized by heats of adsorption less than 10 Kcal/mole, whereas chemisorption is generally accompanied by heats of adsorption of more than 10 Kcal/mol. Generally an ion exchange should occur without any evolution or consumption of heat energy, but in some cases values as high as 10 Kcal/mole has been reported [14]. This large value of heat of adsorption can be explained in terms of chemical processes that may follow an exchange process. Thus heats of adsorption are very helpful in characterizing the adsorbent, especially its suitability for use at a particular adsorption temperature. The negative values of ΔG show that adsorption is spontaneous and these values vary with temperature. At high temperature the ΔG values are more negative and this also indicates increase of adsorption with temperature. Thus our results shows that the adsorption process is more spontaneous at high temperature and is in good agreement with other workers [15-17].

Key words: Adsorption, Zeolites, Inorganic compounds.

TABLE 1. LANGMUIR AND FREUNDLICH PARAMETERS OF ACID RED ADSORPTION ON ZEOLITES.

System	Temperature K	Langmuir Constants 1/K₁K	Vm	Freundlich Constants log K	1/n
Acid red - Zeolite 3A					
	293	0.0957	0.003	1.376	0.90
	298	0.0612	0.005	0.237	0.76
	303	0.359	0.004	1.318	0.85
	308	0.029	0.005	1.300	0.92
Acid red - Zeolite 4A					
	293	0.047	0.003	0.086	0.69
	298	0.031	0.004	0.090	0.94
	303	0.017	0.005	0.016	0.68
	308	0.016	0.006	0.10	0.77

TABLE 2. D-R PARAMETERS FOR ACID RED - ZEOLITE SYSTEM.

System	Temperature (K)	K	Xm	E Kcal/mole
Acid red - Zeolite 3A				
	293	-0.078	0.478	2.52
	298	-0.063	0.391	2.79
	303	-0.620	0.413	2.83
	308	-0.058	0.497	2.91
Acid red - Zeolite 4A				
	293	-0.051	0.266	3.01
	298	-0.050	0.399	3.16
	303	-0.038	0.249	3.58
	308	-0.029	0.234	4.08

TABLE 3. THERMODYNAMIC PARAMETERS OF ACID RED SORPTION ON ZEOLITES.

System	ΔH Kcal/mol	ΔS Kcal/mol.K	Temperature K	$-\Delta G$ Kcal/mol
Zeolite -3A	9.90	0.0495	293	4.60
			298	4.85
			303	5.09
			308	5.35
Zeolite-4A	15.57	0.0696	293	4.82
			298	5.17
			303	5.52
			308	5.87

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