Adsorption of Dyes on Magnesium Hydroxide†

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ABSTRACT: The basic adsorption regularities of water-soluble dyes (acid, direct and basic) on magnesium hydroxide were studied. The dyes were shown to be better adsorbed on magnesium hydroxide precipitated from an aqueous solution of magnesium sulphate than on magnesium hydroxide precipitated from aqueous solutions of magnesium chloride. It was demonstrated thermodynamically that magnesium hydroxide is an effective adsorbent of acid and direct dyes.

INTRODUCTION

Dyes are widely used in the textile industry and they are one of the components of wastewater originating from such industrial enterprises (Timofeeva 1991). Such wastewaters possess a high colour and toxicity since dyes are poisonous compounds with a local action which undergo biochemical oxidation with difficulty. Hence, the removal of dyes from wastewaters arising from textile enterprises constitutes an important ecological problem.

Adsorption provides an effective method for the extensive removal of dyes from wastewaters (Koganovski *et al.* 1990). However, research with such widespread adsorbents as activated carbons has shown that the use of these adsorbents is inadvisable for water-soluble dyes (Klimenko *et al.* 1980). Microporous carbons are not effective since a considerable proportion of their porosity is inaccessible to dye molecules, associates and micelles. The use of macroporous carbons is also not effective because their mechanical strength is limited with a reduction in the possibility of their frequent usage. In addition, activated carbons are expensive and their regeneration involves further financial outlay.

The freely precipitated flocs of aluminium and ferric hydroxides exhibit a macroporous structure and a considerable ability to adsorb dyes (Klimenko *et al.* 1980). However, these adsorbents are most frequently used for the removal of comparatively high concentrations of dyes from wastewaters. Magnesium hydroxide is a similarly cheap and accessible adsorbent that could be used for the removal of dyes from the wastewaters of textile enterprises, although such adsorption behaviour has not been studied to any great extent (Kulski *et al.* 1985).

The present work is an attempt to rectify this omission, with studies of the adsorption regularities of acid, direct and basic dyes on freely precipitated magnesium hydroxide having been undertaken.

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EXPERIMENTAL

Materials

Solutions of $MgCl_2$, $MgSO_4$, NaOH and water-soluble dyes (Acid Orange, Acid Red, Direct Claret, Direct Brown and Methylene Blue) were prepared by dissolving the corresponding salts in distilled water. All chemicals and dyes employed were pure chemically and supplied by the Kyivsky Plant 'RIAP', Cherkassy State Chemical Plant, Rubezhnoe, Ukraine.

Magnesium hydroxide was precipitated from aqueous solutions of $MgCl_2$ and $MgSO_4$ through addition of NaOH solution. The concentrations of all the solutions used were 0.1 N and the pH values of the resulting magnesium hydroxide suspensions were 11.2.

Methods

The following procedure was employed to study the adsorption of the various dyes on the precipitated magnesium hydroxide. Different amounts of dyes (10, 20, 40, 60, 80 and 100 mg/l) were

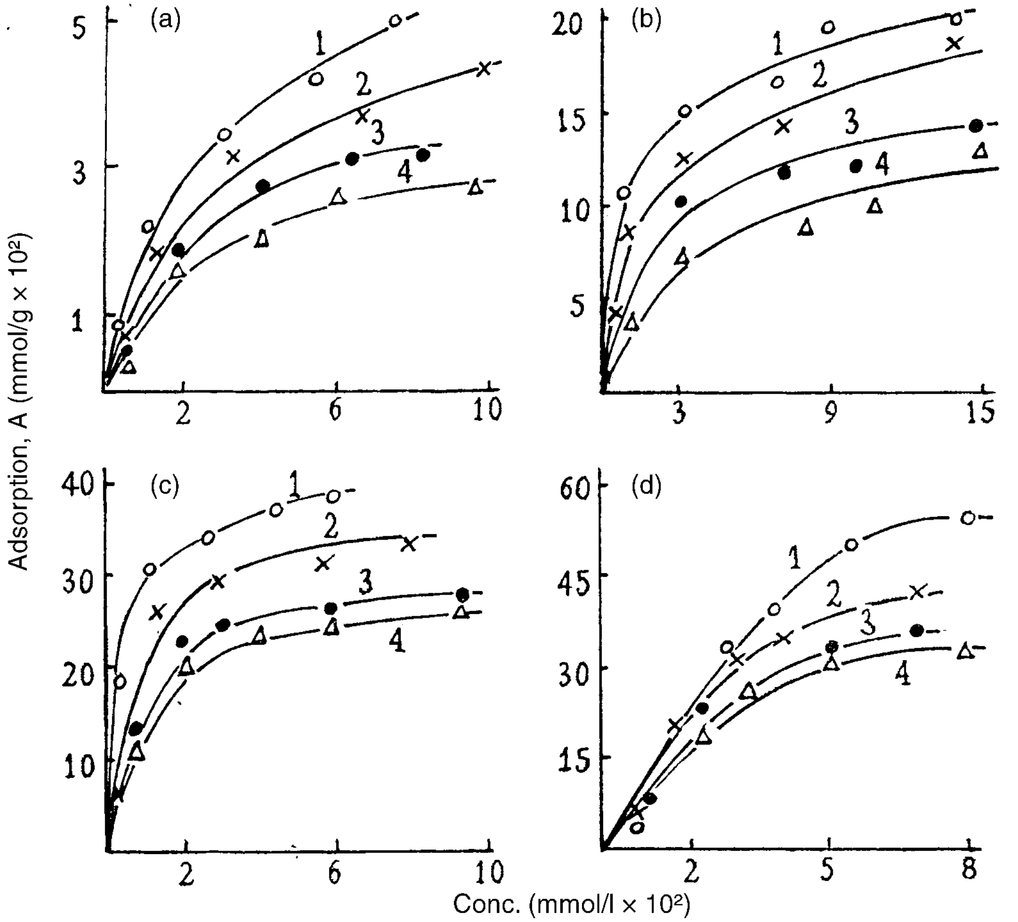

Figure 1. Adsorption isotherms at various temperatures of dyes on magnesium hydroxide precipitated from aqueous solutions of $MgCl_2$. Dyes: (a), Acid Orange; (b), Acid Red; (c), Direct Claret; (d), Direct Brown. Temperatures: 1, 298 K; 2, 303 K; 3, 313 K; 4, 338 K.

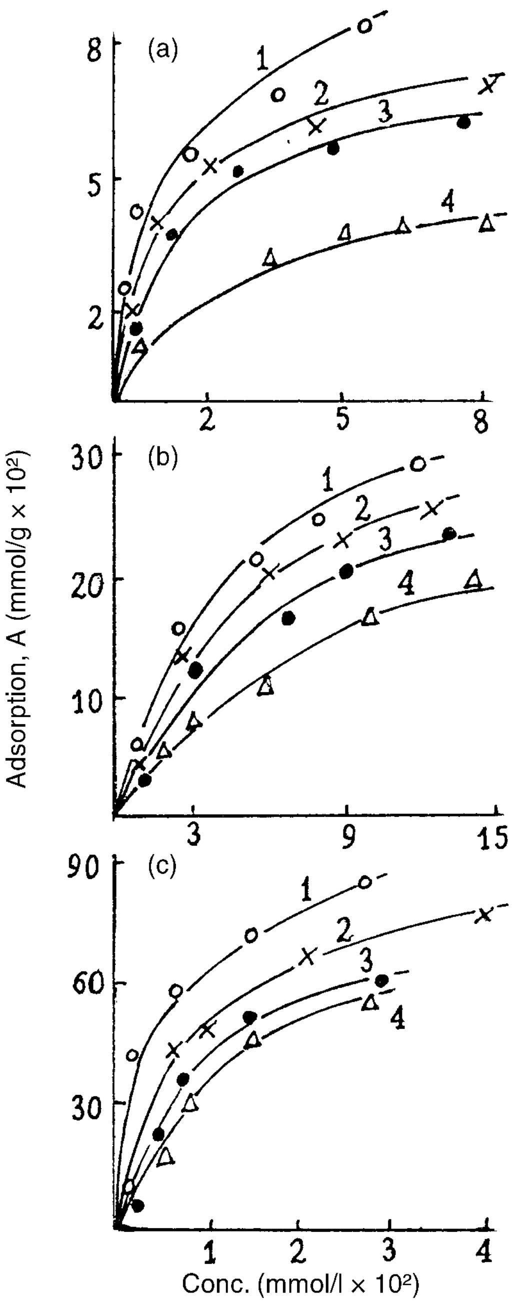

Figure 2. Adsorption isotherms at various temperatures of dyes on magnesium hydroxide precipitated from aqueous solutions of $MgSO_4$. Dyes: (a), Acid Orange; (b), Acid Red; (c), Direct Brown. Temperatures: 1, 298 K; 2, 303 K; 3, 313 K; 4, 338 K.

added as 0.5% solutions to 250 ml volume glass flasks containing 50 ml of a 0.29% suspension of the freely precipitated magnesium hydroxide. Each flask was closed by means of a ground glass stopper and shaken for 30 min in a thermostat at an appropriate temperature in the range 298–

338 K, this time length having been shown to be sufficient for adsorption equilibrium to be attained. After this time, the contents of the flasks were centrifuged for 5 min at 5000 rev/min using a laboratory centrifuge. The separated liquid was analyzed for its dye content spectrophotometrically at an appropriate wavelength.

RESULTS AND DISCUSSION

Adsorption isotherms

Typical adsorption isotherms for the various dyes studied depicted in Figures 1 and 2 indicate that they were all L-type on the basis of the classification of Parfitt and Rochester (1986). It will also be seen from these figures that increasing the temperature of the dye solutions from 298 K to 338 K led to a decrease in the adsorption of acid and direct dyes on magnesium hydroxide precipitated from aqueous solutions of $MgCl_2$ and $MgSO_4$, respectively. It should be noted that Methylene Blue exhibited no adsorption behaviour on precipitated magnesium hydroxide.

Where observed, such a decrease in adsorption with temperature demonstrates the electrostatic (physical) nature of the adsorption forces acting between the adsorbate and adsorbent. In this case, the mechanism of adsorption may be linked to the electrostatic interaction between the organic anions of the direct and acid dyes and the positive charge present on the surface of the precipitated magnesium hydroxide at the pH value (11.2) at which the studies were conducted (Kulski *et al.* 1981).

Comparison of the relative adsorption of acid and direct dyes on magnesium hydroxide precipitated from aqueous solutions of $MgSO_4$ and $MgCl_2$ demonstrated that the former when employed as adsorbent exhibited higher adsorption characteristics. This was attributed to the crystallinity of the flocs precipitated from these two solutions, with those obtained from $MgSO_4$ solutions providing a greater surface area relative to those obtained from $MgCl_2$ solutions.

Thermodynamics of adsorption

The thermodynamic adsorption parameters associated with dye–magnesium hydroxide systems have not been determined previously but they are of practical importance since the values of ΔG may be employed as a reliable criterion for adsorption efficiency.

The adsorption isotherms depicted in Figures 1 and 2 may be described by the Langmuir equation, thereby allowing the values of the β and A_∞ constants associated with this equation to be determined. In addition, the adsorption equilibrium constant (K) defined as:

$$K = \beta\gamma \frac{S_0}{S} \tag{1}$$

TABLE 1. Maximal Values of Surface Area Occupied by Dye Molecules (Ions)

Dye molecule	Surface area occupied, S_0 (nm^2)
Acid Orange	1.15
Acid Red	1.26
Direct Brown	2.45
Direct Claret	2.73

TABLE 2. Thermodynamic and Langmuir Constants for Adsorption of Various Dyes on Magnesium Hydroxide

Dye	Magnesium salt employed for $Mg(OH)_2$ precipitation	Temp. (K)	β (l/mmol)	K (l/mmol)	$10^3 A_\infty$ (mmol/g)	$-\Delta G$ (kJ/mol)	ΔH (kJ/mol)	ΔS [J/(mol K)]
Acid Orange	$MgCl_2$	298	58.33	271.40	5.7	31.00	10.97	140
		303	68.33	317.64	4.9	31.91		
		313	84.62	393.33	3.9	33.53		
		338	108.33	503.58	3.1	36.90		
Acid Red		298	20.00	84.82	25.0	28.12	10.81	130
		303	20.63	87.47	24.2	28.67		
		313	25.00	106.03	20.0	30.11		
		338	32.61	138.30	15.0	33.26		
Direct Claret		298	235.29	459.97	42.5	31.44	9.07	140
		303	290.00	565.80	34.5	33.37		
		313	340.00	663.34	29.4	34.88		
		338	344.44	672.03	29.0	37.71		
Direct Brown		298	180.00	391.10	55.6	31.90	8.31	140
		303	225.00	489.00	44.4	33.00		
		313	250.00	543.33	40.0	34.36		
		338	280.00	608.53	35.7	37.43		
Acid Orange	$MgSO_4$	298	120.48	560.05	8.3	32.79	15.01	160
		303	125.00	581.05	8.0	33.44		
		313	150.00	697.26	6.7	35.01		
		338	240.00	1115.62	4.2	39.13		
Acid Red		298	25.00	106.03	40.0	28.67	19.12	160
		303	25.00	106.03	40.0	29.15		
		313	41.67	176.71	24.0	31.44		
		338	50.00	212.05	20.0	34.47		
Direct Brown		298	133.33	289.78	125.0	31.16	9.98	140
		303	188.89	410.52	88.2	32.56		
		313	233.33	507.11	71.0	34.19		
		338	233.33	507.11	71.0	37.00		

may be obtained, where γ is the number of moles of solvent in 1 kg of its mass (for water, γ = 55.5 mol/kg) and S_0 and S are the areas occupied, respectively, by the solvent molecules and dye ions on the adsorbent surface. The value of S_0 employed was 0.0959 nm^2 (Skrylev and Streltsova 1980) while the maximum possible values of S for the dye molecules were obtained via molecular mechanics employing an MM parameterization method. The corresponding values are listed in Table 1.

The various thermodynamic parameters were calculated using the following equations:

$$\Delta G = -RT \ln K \tag{2}$$

$$\Delta H = RT^2 \frac{d \ln K}{dT} \tag{3}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

where ΔG is the free energy associated with adsorption, ΔH is the adsorption enthalpy and ΔS is the adsorption entropy.

The various values of A_∞ (determined experimentally), ΔG, ΔH and ΔS for the dye–magnesium hydroxide systems studied are listed in Table 2. From the data listed, it will be seen that the values of $-\Delta G$ obtained for the various systems lay in the range 28.12–39.13 kJ/mol indicating that the adsorption process was favoured under the experimental conditions employed, those for ΔH were positive (indicating that the process was endothermic) and lay in the range 8.31–19.12 kJ/mol, while those for ΔS were also positive and were equal to 130–160 J/(mol K).

CONCLUSIONS

The following conclusions may be drawn from the work described:

1. The adsorption of acid and direct dyes on magnesium hydroxide occurs through electrostatic attraction and is therefore physical in nature.
2. Magnesium hydroxide precipitated from an aqueous solution of $MgSO_4$ was more effective as an adsorbent than magnesium hydroxide precipitated from an aqueous solution of $MgCl_2$.
3. The various thermodynamic parameters calculated support the fact that magnesium hydroxide is an effective adsorbent for the removal of acid and direct dyes from aqueous solutions.

REFERENCES

Klimenko, N.A., Lupashku, F.G. and Koganovski, A.M. (1980) *Kolloidn. Zh.* **42**, 135.
Koganovski, A.M., Klimenko, N.A., Levchenko, T.M. and Roda, I.G. (1990) *Adsorption of Organic Substances from Water*, Khimia, Leningrad.
Kulski, L.A., Shkavro, Z.N., Medvedev, M.I., Reznik, B.I. and Bagnyuk, V.M. (1981) *J. Water Chem. Technol.* **3**, 461 (in Russian).
Kulski, L.A., Kruglitski, N.N., Ivanuk, A.A. and Pakhovchishin, S.V. (1985) *J. Water Chem. Technol.* **7**, 44 (in Russian).
Panchenko, N.P. and Klimenko, N.A. (1976) *Kolloidn. Zh.* **38**, 999.
Parfitt, G.D. and Rochester, C.H. (1986) *Adsorption from Solution at the Solid/Liquid Interface*, Mir, Moscow.
Skrylev, L.D. and Streltsova, E.A. (1980) *Kolloidn. Zh.* **42**, 594.
Timofeeva, S.S. (1991) *J. Water Chem. Technol.* **13**, 550 (in Russian).