Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kaneko, Shoji(1982) 'Adsorption of Several Dyes from Aqueous Solutions on Silica-Containing Complex-Oxide Gels', Separation Science and Technology, 17: 13, 1499 — 1510

To link to this Article: DOI: 10.1080/01496398209438469

URL: http://dx.doi.org/10.1080/01496398209438469

SEPARATION SCIENCE AND TECHNOLOGY, 17(13 & 14), pp. 1499–1510, 1982-83

Adsorption of Several Dyes from Aqueous Solutions on Silica-Containing Complex-Oxide Gels

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Abstract

Removal of dyes from aqueous solutions was investigated in a batchwise operation using binary or ternary silica-containing complex-oxide gels as adsorbents. The following three combinations of gels showed the best results: (1) silica-titania-magnesia gel for C.I. Acid Blue 40, (2) silica-titania gel for C.I. Basic Blue 3, and (3) silica-titania gel treated with alkali for C.I. Reactive Red 5. The adjustment of the initial pH of the dye solution was effective in all cases. Freundlich-type adsorption isotherms related the amount of dye adsorbed to its equilibrium concentration in solution. The gels which adsorbed the dye abundantly were effectively regenerated for reuse by heating them at 600°C, which caused decomposition of the dye.

INTRODUCTION

Dyeing wastewater, containing various substances which are responsible for coloration, eutriphication, and consumption of dissolved oxygen, has most commonly been treated by coagulation or activated sludge processes. However, soluble components such as reactive dyes in the wastewater cannot be removed adequately, so that an improved procedure is necessary to permit reuse of this water as well as to avoid damage to the aquatic environment. Adsorption processes seem to be effective for the removal of water pollutants at low concentrations, and they seldom cause secondary pollution because they do not form sludges and the adsorbents used are usually easily regenerated. Using such a process as a polishing technique after any conventional process may well become the most feasible technique among various advanced treatment methods for these wastewaters. For this to be practical, however, excellent adsorbents from both functional and economical standpoints are essential.

Although activated carbon (*1*), clay (*2*), ion-exchange resin (*3*), peat (*4*), wood (*5*), silica (*6*), and zirconium hydroxide (*7*) have been tested as adsorbents, none of them has been shown to be appropriate for the removal of dyes from aqueous solutions. The adsorption mechanisms are not at all well-understood, although some explanations have been given for activated carbon (*1*), clay (*2*), and zirconium hydroxide (*7*).

We earlier reported that silica-titania complex-oxide gel prepared by a homogeneous precipitation method was a porous material stable at temperatures above 600°C, and that it possessed favorable properties as a catalyst and an adsorbent (*8–10*). The present paper deals with the investigation of the adsorptive abilities of binary and ternary silica-containing complex-oxide gels for several dyes in aqueous solutions by means of a batch equilibration test, and also with the study of the regeneration of the adsorbents used on the basis of their thermal stability.

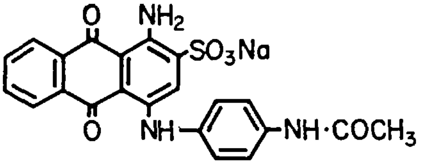
EXPERIMENTAL

Materials

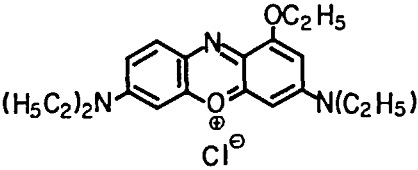
A complex-oxide gel was homogeneously precipitated from a mixture of sodium metasilicate solution acidified with hydrochloric acid, metal chloride (metal: Ti, Al, or Mg), and urea by heating at 90°C for 5 h. The precipitate was washed after filtration with deionized water until neither ammonium ion nor chloride ion was detected in the washings, and then it was dried at 110°C overnight. The ratio of silica to metal oxide was 1:1 for the composition of a binary compound and that of silica to two metal oxides was 2:1:1 in a ternary compound. Heating the dried gel at 600°C for 1 h, followed by granulation to the size of ~0.5 mm gave the adsorbent. Alkali treatment of the adsorbent was carried out by immersion in 1 *N* sodium hydroxide solution at 20°C for 24 h, after which the adsorbent was thoroughly washed with deionized water.

Methods

Laboratory tests on three commercially available dyes, C.I. Acid Blue 40 (Kayacyl Blue AGG, Nippon Kayaku Co., Ltd.),



C.I. Basic Blue 3 (Doerlene Blue 5G, Ciba-Geigy),



and C.I. Reactive Red 5 (Mikacion Red GS, Nippon Kayaku Co., Ltd.), a monoazo-dichlorotriazinyl compound of which more detailed structure or chemical name is unknown, were conducted by shaking 0.2 g of adsorbent with 50 mL of dye solution (concentration of 100 mg/L) for various contact time (10 min to 24 h). After agitation, 5 mL of the solution was pipetted off and filtered through a 0.45-μm membrane filter. The concentration of dye was then determined using a Shimadzu Model RC-330 spectrophotometer with a 5-mm light path cell. The rate of color removal was obtained from the time dependence of the ratio of the area in the absorption spectrum between 400 and 700 nm of the sample to that of the spectrum of the solution before treatment. Adjustment of the initial pH of dye solution was achieved by adding hydrochloric acid or sodium hydroxide solution. The variation of the spectrum of every solution by this adjustment was negligible. Both differential thermal analysis and thermogravimetry of the adsorbent used were simultaneously performed using a Rigaku thermoanalysis apparatus; the heating rate was 5°C/min in air, with α-Al_2O_3 as a reference substance.

RESULTS AND DISCUSSION

Adsorption of C.I. Basic Blue 3 on Various Complex-Oxide Gels

All the gels adsorbed C.I. Basic Blue 3 to a certain extent after prolonged shaking. Silica-titania and silica-titania-magnesia gels possessed excellent adsorptive abilities, and 100% color removal from the dye solution resulted after shaking for 2 and 3 h, respectively, as shown in Fig. 1. Silica-titania-alumina gel adsorbed well; the extent of color removal attained ~100% after

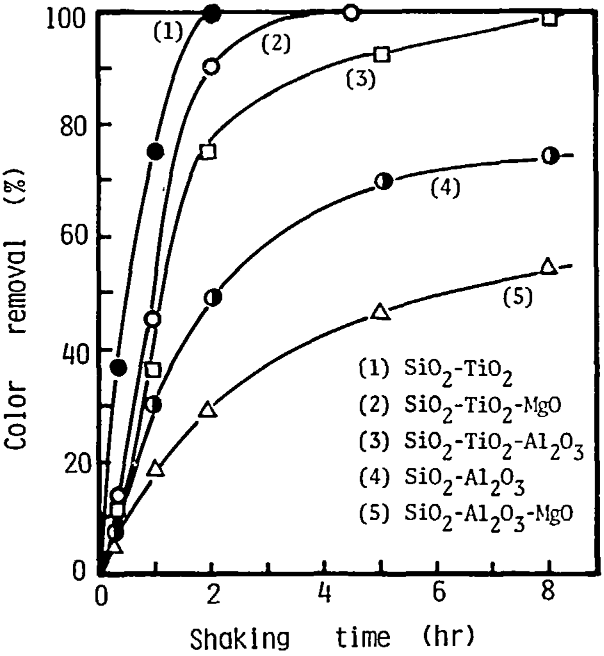


FIG. 1. Adsorption of C.I. Basic Blue 3 on various silica-containing complex-oxide gels.

8 h. Silica-alumina and silica-alumina-magnesia gels showed slower rates of color removal than the others; the dye solutions were still colored after the test.

The properties of the adsorbents used are given in Table 1. The surface areas of the silica-titania-alumina, silica-alumina, and silica-alumina-magnesia gels were 244, 226, and 148 m^2/g, and their bulk densities were 0.44, 0.54, and 0.36 g/cm^3, respectively. These gels were all composed of porous material having large surface areas; nevertheless, differences among their adsorptive abilities appeared. It is assumed that the adsorption of the dye depends on the surface properties arising from the composition, the preparation method, and the heat treatment rather than on the surface solid structure related to physical adsorption.

Effect of Initial pH

The relationship between initial pH and the adsorption of the dye on the gel was examined (Figs. 2 and 3) because it was known that adsorption from

TABLE 1
Properties of Representative Adsorbents Used

Adsorbent	Bulk density (g/cm^3)	Specific surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)		Mean diameter of micropore (Å)	Acid amount[c] (mmol/g)		
			Total	Less than 200 Å		p$K_a \leqq 7.1$	p$K_a \leqq 4.0$	p$k_a \leqq 1.5$
Silica-titania	0.38	240	1.45	0.54	140	0	0.95	0.60
Silica-titania-magnesia	0.55	310	1.46	0.97	85	0	0.58	0.30
Alkali-treated silica-titania	0.59	268	0.62	0.34	80	0.98	0	0

[a] By BET method.
[b] By mercury penetration porosimetry.
[c] By amine titration method.

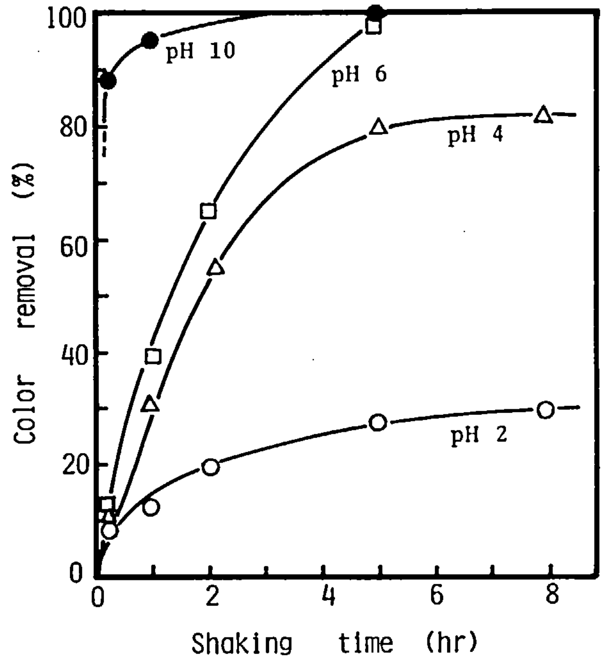


FIG. 2. Effect of initial pH on adsorption of C.I. Basic Blue 3 on silica-titania gel.

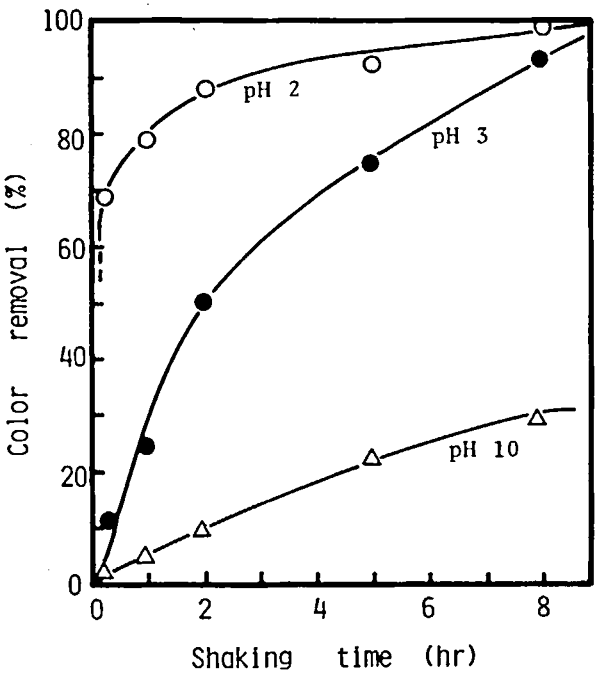


FIG. 3. Effect of initial pH on adsorption of C.I. Acid Blue 40 on silica-titania-magnesia gel.

aqueous solution is often affected by initial pH (*10, 11*). The rate of color removal increased with an increase of pH for the adsorption of C.I. Basic Blue 3 on silica-titania gel. With a pH of 4.5 in the original solution, color removal reached 95% at pH 6 after 5 h and 90% at pH 10 after only 10 min. Accurate data under more basic conditions could not be obtained owing to the flocculation of the dye at pH values above 10. Silica-titania-magnesia gel was more effective than silica-titania gel in the adsorption of C.I. Acid Blue 40. The rate of color removal by adsorption of the dye on silica-titania-magnesia gel increased with decreasing pH. With a pH of 6 in the original solution, color removal reached 72% after 10 min and ~100% after 8 h at pH 2.

In this manner it was proved that either silica-titania gel or silica-titania-magnesia gel adsorbed both C.I. Acid Blue 40 and C.I. Basic Blue 3 as well, and that suitable values of pH were around 2 for C.I. Acid Blue 40 and more than 4 for C.I. Basic Blue 3, respectively; these pH values are almost the same values as are used for the dyeing in practice. This suggests that the adsorption mechanism may be similar to that involved in the dyeing process, including any activation or association of the dye. The surface area, the pore volume, and the pore diameter of the gels, all related to physical adsorption, are large; however, the differences in these values between the two gels are not so appreciable (Table 1). Silica-titania gel shows a high solid acidity as reported by Tanabe et al. (*12, 13*), and silica-titania-magnesia gel also shows a solid acidity. There is no appearance of solid basicity upon addition of magnesia to silica-titania gel. Both the cation- and anion-exchange abilities of titania gel have hitherto been known, as well as the cation-exchange ability of silica gel (*14*). Kawasaki reported that silica-titania gel showed some cation-exchange capability (*15*). The adsorptions of the acid and the basic dyes on kaolinite or montmorillonite were explained on the basis of an ion-exchange reaction (*2*). It is therefore presumed that the adsorptive abilities of the gels showing both cation- and anion-exchange properties in aqueous solution are due to the same reaction:

At lower pH values,

$$\text{D-SO}_3^- + \text{HMOH} \rightarrow \text{D-SO}_3 \cdot \text{MH} + \text{OH}^- \qquad (1)$$

At higher pH values,

$$\text{D-NR}_3^+ + \text{HMOH} \rightarrow \text{D-NR}_3 \cdot \text{MOH} + \text{H}^+ \qquad (2)$$

where D is a dye matrix and M is a metal ion.

Adsorption Isotherm

Fifty milliliter portions of the solutions containing C.I. Acid Blue 40 or C.I. Basic Blue 3 (concentrations of 60, 80, 100, 150, and 200 mg/L) were shaken to reach equilibrium with 0.1 g of adsorbent at each optimum pH for 24 h. The amount of adsorption was related to the equilibrium concentration by a Freundlich-type adsorption isotherm, Eq. 3 (Fig. 4), and the data obtained are shown in Table 2:

$$x = Kc^{1/n} \qquad (3)$$

where x is the amount of adsorption (mg dye/g adsorbent), c is the concentration at equilibrium (mg/L), and K and n are constants. The high adsorptive capacity of silica-titania gel appears at low concentrations, and that of silica-titania-magnesia gel shows up at relatively high concentrations.

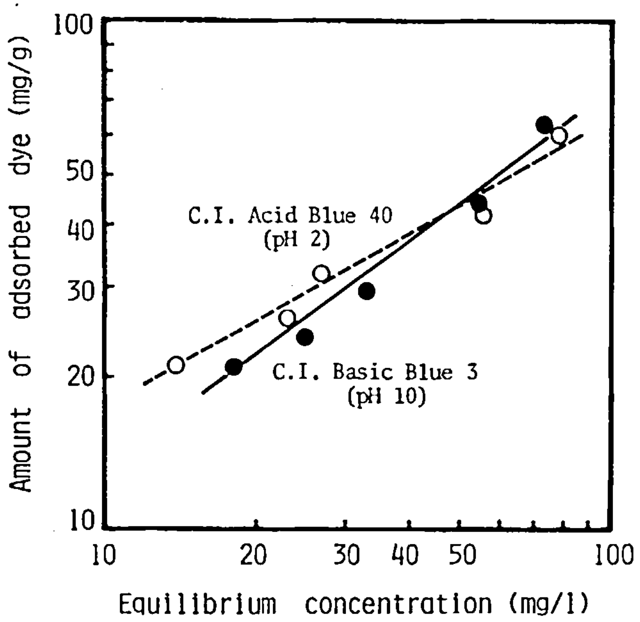


FIG. 4. Adsorption isotherm of C.I. Acid Blue 40 and C.I. Basic Blue 3 on silica-titania gel.

Adsorption of C.I. Reactive Red 5

Removal of a hydrophilic reactive dye in wastewater by means of a conventional process is most difficult. This prompted the investigation of the adsorption of C.I. Reactive Red 5 on silica-titania gel, which was carried out after a preliminary test (Fig. 5). The adjustment of the initial pH of the dye solution was effective in a manner similar to that found with the other dyes, as shown in Figs. 2 and 3. The greatest extent of color removal was

TABLE 2
Data on Adsorption Isotherm ($x = Kc^{1/n}$) of Dye on Complex-Oxide Gel

Adsorbent	C.I. name	Initial pH	K	$1/n$	Amount of adsorbed dye at an equilibrium concentration of 10 mg dye/L solution (mg dye/g adsorbent)
Silica-titania	Acid Blue 40	2	5.0	0.50	17.5
	Basic Blue 3	10	2.4	0.67	13.0
Silica-titania-magnesia	Acid Blue 40	2	0.54	1.48	9.3
	Basic Blue 3	10	0.13	0.60	2.4

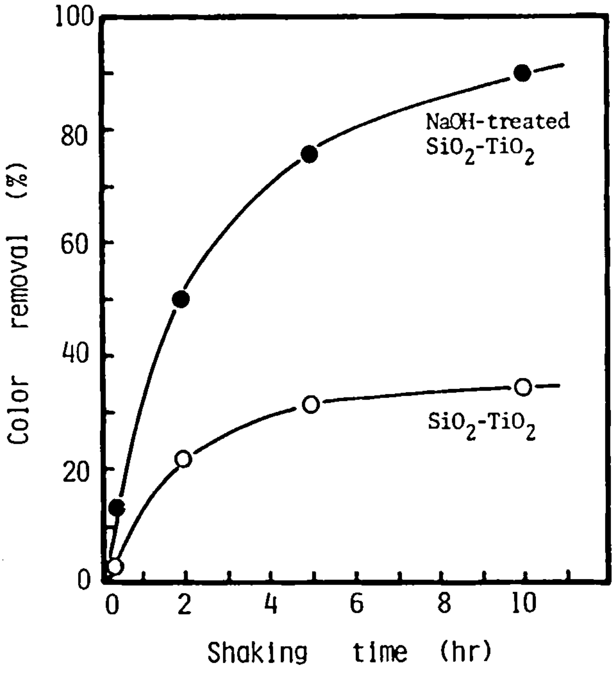


FIG. 5. Adsorption of C.I. Reactive Red 5 on silica-titania gels.

nevertheless only 32% at pH 1 after 10 h. When alkali treatment of the gel was carried out as described in a previous paper (*10*), its adsorptive ability was remarkably improved, so that 88% color removal was obtained under the same conditions. The surface properties of the gel were considerably changed by the alkali treatment, e.g., the pore diameter was reduced from 140 to 80 Å, closer to the size of the dye molecule, as shown in Table 1. Accordingly, the affinity of the gel for the dye presumably increased, thereby improving its adsorptive ability.

Regeneration of the Adsorbents

Figure 6 shows the results of thermogravimetric analysis of the gels used. A silica-titania-magnesia gel which adsorbed C.I. Acid Blue 40 abundantly gave a total weight loss of 17.2% on heating to 600°C. The weight loss is attributed to the release of water (15%) at 150°C and the decomposition of the dye (2.2%) above this temperature. Further, a silica-titania gel used to adsorb C.I. Basic Blue 3 showed a weight loss of 7.3%, 5% loss of water at 150°C and 2.3% loss of the dye above this temperature. In the DTA curves

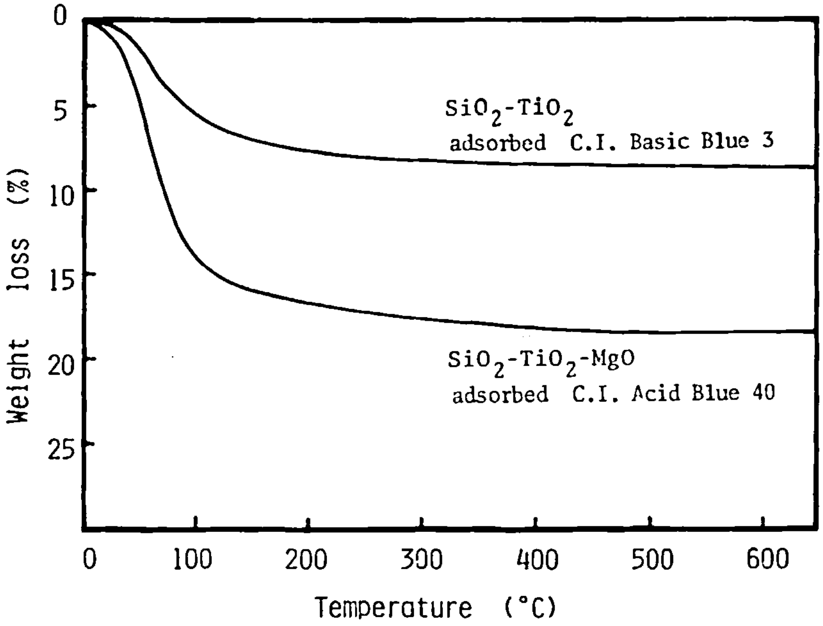


Fig. 6. Thermogravimetric curves of adsorbents used.

of the gels used, only a single broadly endothermic peak was seen at around 150°C, and no clear peak corresponding to the decomposition of the dye was found. The gels used for the thermal analysis were colored dark blue by the adsorption of the dyes at first; however, the colors returned completely to the original white at the end of the analysis. On the basis of this fact, a silica-titania gel which had been used once was heat-treated at 600°C for 30 min and then it was immersed in dye solution again to test its adsorptive ability. Its adsorptive capacity was regenerated completely; there was no difference between it and that of fresh gel in the rate of color removal. The used gel was satisfactorily regenerated by the thermal decomposition of the adsorbed dye. After four cycles of adsorption and regeneration, the adsorptive capacity had not fallen at all. The surface area of silica-titania gel was reduced somewhat (from 240 to 215 m^2/g) after adsorption of the dye, although this value rose to 238 m^2/g after thermal decomposition of the adsorbed dye. The regeneration of the gel may be predicted not only by the change of coloration but also by the lack of change in the surface area resulting from the thermal stability of the gel itself (*8*). This finding was quite analogous to that in silica-titania-magnesia gel.

CONCLUSION

The following combinations were best among those examined: silica-titania-magnesia gel for C.I. Acid Blue 40, silica-titania gel for C.I. Basic Blue 3, and alkali-treated silica-titania gel for C.I. Reactive Red 5. In all cases the adjustment of the initial pH of the dye solution was effective. Color removals to the extent of 72% after 10 min and ~100% after 8 h at pH 2 were obtained in the treatment of the acid dye solution with silica-titania-magnesia gel. Color removal from the basic dye solution reached 88% at pH 10 after 10 min with silica-titania gel. The amount of adsorption was related to the equilibrium concentration in the adsorption of either the acid or the basic dyes on both gels by Freundlich-type adsorption isotherms. Alkali-treated silica-titania gel removed 90% of the reactive dye from aqueous solution at pH 1 after 10 h. When the gels were heated at 600°C after being saturated with dye, their adsorptive capacities regenerated completely; this was accompanied by the thermal decomposition of the dye. It was possible to use the regenerated gels repeatedly.

Acknowledgments

The author wishes to thank Professor Fumio Imoto for his provision of facilities and is deeply indebted to Messrs Tadahiko Miyamoto and Shigeo Kinoshita for technical assistance during the course of this work.

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Received by editor December 11, 1981
Revised May 3, 1982