

Removal of Water-Soluble Cationic Dyes with TriSyl Silicas

Erdener KARADAĞ

Adnan Menderes University,

Chemistry Department, 09010 Aydın-TURKEY

Dursun SARAYDIN

Chemistry Department

Cumhuriyet University, 58140 Sivas-TURKEY

Fatma AYDIN

Mersin University,

Chemistry Department, 33000 Mersin-TURKEY

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In this study, the adsorption of certain water-soluble cationic dyes, (basic blue 9, basic blue 12, basic blue 17, brilliant cresyl blue, janus green B, basic green 4, basic violet 1, basic violet 3, and thionin) onto TriSyl silicas by batch adsorption at 25° C was investigated. In the adsorption experiments, Langmuir type adsorption in the Giles classification system was found. Binding parameters such as the initial binding constant (K_i), the equilibrium binding constant (K), monolayer coverage(n), site-size(u), maximum fractional occupancy ($\hat{\theta}$), and the thermodynamic parameter free energy of adsorption (ΔG) were calculated for TriSyl silica and cationic dye systems by using the linearization methods of Klotz and Langmuir.

Key words: TriSyl silicas, cationic dyes, binding, adsorption

Introduction

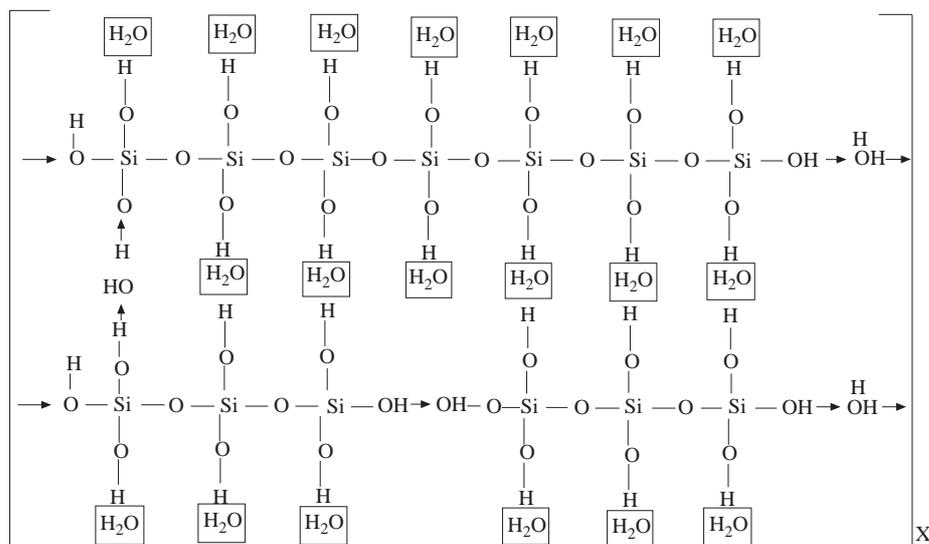
The cleaning of waste and waste water is one of most serious environmental problems of the present day. Discoloration in drinking water may be due to the presence of coloured organic substances or highly coloured industrial wastes, of which pulp, paper and textile wastes are common. Highly coloured, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is known. The organic colouring materials in water stimulate the growth of many aquatic micro-organisms¹.

Synthetic dyes represent a relatively large group of organic chemicals which are encountered in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on humans. In order to minimize the possible damage to people and the environment arising from the production and applications of dyes, several studies have been done around the world. The potential toxicity of certain azo dyes has been known for many decades. Other azo dyes are no longer in use since they are carcinogenic. Disazo dyes based on benzidine are also known to be

carcinogenic².

TriSyl is the commercial name of a silica gel. Silica gel is an amorphous synthetic form of silicon dioxide produced under carefully controlled conditions in order to achieve specific adsorbing properties. TriSyl silicas are odourless, tasteless, free flowing white powders with a high degree of purity, greater than 99.0 % silicon dioxide (when dry). It is known that TriSyl silicas are selective and highly efficient adsorbents of phosphatides, trace metals (notably copper and iron), soaps and oxidation compounds from glyceride oils in the oil refining industry³. The chemical structure of TriSyl is shown in Scheme 1.

In our previous studies, we have investigated the absorption of uranyl ions⁴, some heavy metal ions⁵ and some water-soluble cationic dyes⁶⁻⁹ through acrylamide/itaconic acid and acrylamide/maleic acid hydrogels and the binding of certain anionic dyes onto crosslinked poly(N-vinyl pyrrolidone)¹⁰⁻¹¹.



Scheme 1. The chemical structure of TriSyl silicas.

In this study, the adsorption of certain water-soluble cationic dyes, namely basic blue 9 (methylene blue), basic blue 12 (nil blue), basic blue 17 (toluidin blue), brilliant cresyl blue, janus green B (union green B), basic green 4 (malachite green), basic violet 1 (methyl violet), basic violet 3 (crystal violet), and thionin (lauths violet), were investigated by using a new synthetic silica gel (TriSyl). These water-soluble cationic dyes resemble the large molecular dyes found in waste waters, and they are toxic and carcinogenic.

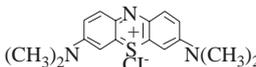
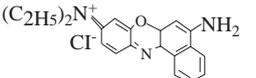
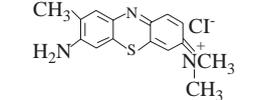
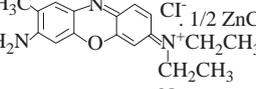
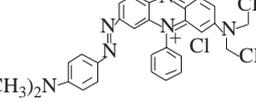
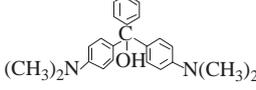
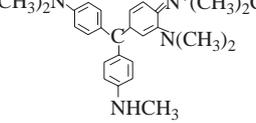
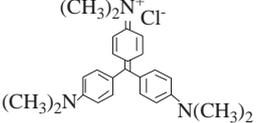
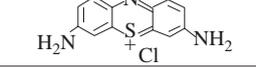
Experimental

TriSyl silicas were obtained from Grace Speciality Chemical Co. (Germany). Basic blue 9 (BB 9), basic blue 12 (BB 12), basic blue 17 (BB 17), brilliant cresyl blue, (BCB), janus green B (JG B), basic green 4 (BG 4), basic violet 1 (BV 1), basic violet 3 (BV 3), and thionin (T) were purchased from Sigma (St. Louis, USA). The chemical formulas and other properties of the dyes are shown in Table 1.

Synthetic aqueous solutions of the dyes were prepared in the desired concentrations. TriSyl silicas weighing 0.1 g were transferred into 50 ml of aqueous solutions of the aqueous dye solution and allowed to equilibrate for two days at 25 °C in a water bath. The times of adsorption equilibrium were determined at the end of the preexperimental studies. Supernatants of these solutions were separated by decantation and centrifugation from TriSyl silicas. Spectrophotometric measurements were carried out using a Shimadzu 160

A model UV-VIS spectrophotometer at ambient temperature. The absorbances of these supernatants are shown at the suitable wavelengths in Table 1. Distilled water was chosen as the reference. The equilibrium concentrations of the water soluble cationic dye solutions were determined by means of precalibrated scales.

Table 1. Some Properties of the Dyes.

Name	Chemical Formula	Molar Mass	Cl Nr.	λ_{\max}/nm
Basic blue 9		373.90	52 015	661
Basic Blue 12		354.92	51 180	600
Basic Blue 17		305.83	52 040	626
Brilliant Cresyl Blue		385.96	51 010	622
Janus Green B		511.07	11 050	660
Basic Green 4		346.48	42 000	617
Basic Violet 1		393.96	42 535	560
Basic Violet 3		407.99	42 535	588
Thionin		287.34	52 000	598

For the investigation of the influence of mass of TriSyl silicas on dye adsorptions, synthetic aqueous solutions of the dyes were prepared in constant concentrations of 10 mg BB 9 L⁻¹, 25 mg BB 12 L⁻¹, 25 mg BB 17 L⁻¹, 25 mg BCB L⁻¹, 80 mg JG B L⁻¹, 15 mg BG 4 L⁻¹, 20 mg BV 1 L⁻¹, 5 mg BV 3 L⁻¹ and 15 mg T L⁻¹. TriSyl silicas of increasing mass were transferred into 50 ml of aqueous solutions of the aqueous dye solutions and allowed to equilibrate for two days at 25°C in a water bath.

Results and Discussion

Binding of Dyes onto TriSyl Silicas

To observe adsorption of some water-soluble cationic dyes, TriSyl silicas were placed in synthetic aqueous solutions of the cationic dyes BB 9, BB 12, BB 17, BCB, JG B, BG 4, BV 1, BV 3 and T, and in synthetic aqueous solutions of the anionic dyes such as alizarin yellow G, titan yellow, Congo red, methyl orange,

Evans blue, naphthol green B, and azocarmin B, and allowed to equilibrate for two days. At the end of this time, TriSyl silicas in the cationic dye solutions showed the dark colorations of the colours of the original solutions, whereas TriSyl silicas in the anionic dye solutions did not.

The interactions between cationic dyes and TriSyl silicas may be electrostatic interactions. Electrostatic interactions may have occurred between positive charges of the water-soluble cationic dyes and oxygen atoms and hydroxyl groups in the TriSyl silicas. However, hydrogen bonds would be expected to occur between amine groups in the dye molecules and the oxygen atoms and hydroxyl groups in the TriSyl silicas. On the other hand, there should be anionic repulsion between negative charges of anionic dyes and oxygen atoms and hydroxyl groups in the TriSyl silicas and, therefore little interaction between the anionic dyes and TriSyl silicas^{12,13}.

Binding Isotherms of Dyes onto TriSyl Silicas

In order to observe the uptake of the water-soluble cationic dyes, TriSyl silicas were placed in aqueous solutions of the cationic dyes and allowed to equilibrate for two days. At the end of this time, TriSyl silicas in the aqueous solutions of cationic dyes displayed darker colorations of the original solutions.

In a batch adsorption system at equilibrium, the total solute concentration (C_I , mol L⁻¹) is

$$C_I = C_B + C \quad (1)$$

where C_B is the equilibrium concentration of the solute in the adsorbent in mol L⁻¹ (bound solute concentration) and C is the equilibrium concentrations of the solute in the solution in mol L⁻¹ (free solute concentration)¹². The value of the bound concentration may be obtained by difference with Eq. 1. For a fixed free solute concentration, C_B is proportional to the polymer (silicagel) concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio, r , defined by

$$r = C_B/P. \quad (2)$$

Thus with C_B in mol L⁻¹ and P in base mol (moles of monomer units) L⁻¹, r then represents the average number of molecules of solute bound per monomer unit at that free solute concentration¹⁴.

Plots of the binding ratio (r , mol dye/mol monomeric unit of silicagel) against the free concentrations of the dyes in the solutions (C , μ mol dye L⁻¹) are shown in Fig. 1.

Figure 1 shows that adsorption of the dye within TriSyl silicas corresponds to type L (*Langmuir type*) [BB 9, BB 12, BB 17, BCB, JG B, and BV 1 corresponds to type L2, whereas BG 4, BV 3 and T correspond to type L3] adsorption isotherms in the Giles classification system for adsorption of a solute from its solution¹⁵⁻¹⁷.

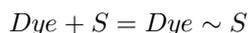
In this type adsorption isotherm, the initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent¹⁵⁻¹⁷.

The types of system which give this curve do in fact fulfill these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition. Examples of (ii) are (a) systems with highly polar solute and adsorbent, and a non-polar solvent, and (b) systems in which monofunctional ionic substances with very strong intermolecular attraction are adsorbed from water by ion-ion attraction. It is possible that in these cases (system b) the adsorbed ions may have become associated into very large cluster as adsorption took place¹⁵.

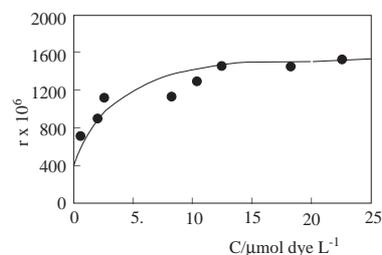
The binding data were interpreted on the basis of the uniform site-binding model (u.s.b.), which in statistical-thermodynamic terms corresponds to the formation of an ideal localised one-dimensional monolayer of solute on the polymer chains¹⁴. This leads to the hyperbolic (*Langmuir*) form of binding isotherm, which applies to many polymer/solute binding systems:

$$r = \frac{nKC}{1 + KC} \quad (3)$$

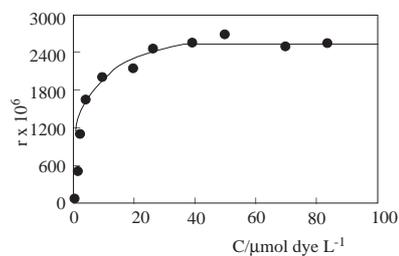
where K is the binding constant, i.e., the equilibrium constant for the attachment of a molecule of dye onto a site S by a specific combination of non-covalent forces:



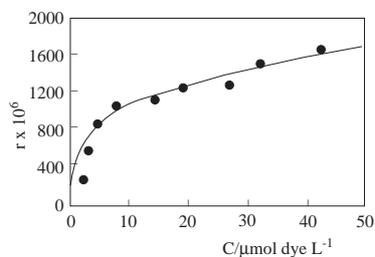
and n (mol dye/mol monomeric unit of polymer) is the site density, i.e., the limiting value of r for *monolayer* coverage, which is thus a measure of the density of sites S along the silicagel chain. The reciprocal of n is the site-size, u (mol monomeric unit of silicagel / mol dye), which may be taken to represent either the average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain saturated.



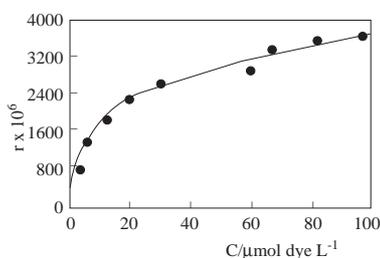
i. Basic Blue 9



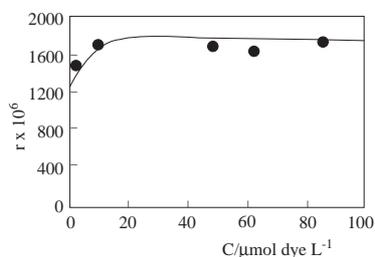
i. Brilliant Cresyl Blue



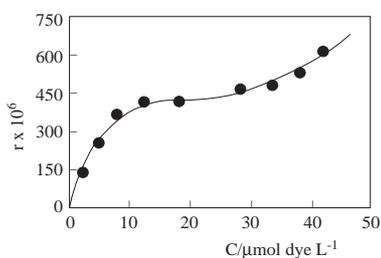
ii. Basic Blue 12



ii. Janus Green B



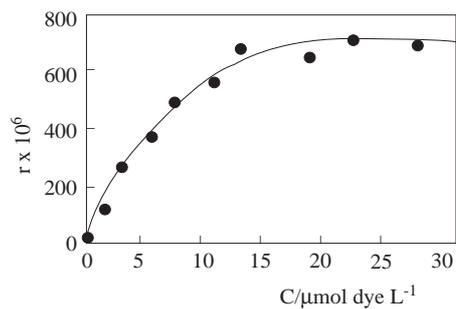
iii. Basic Blue 17



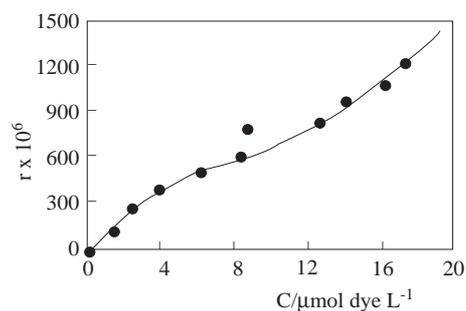
iii. Basic Green 4

Figure 1a. Binding isotherms of TriSyl Silicas/Dye Systems.

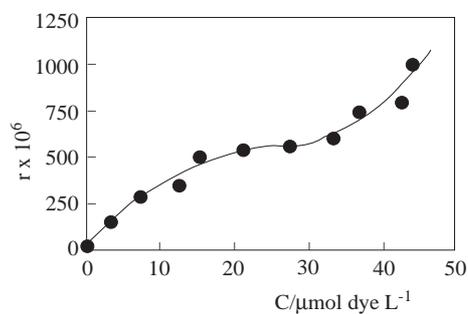
Figure 1b. Binding isotherms of TriSyl Silicas/Dye Systems.



i. Basic Violet 1



ii. Basic Violet 3



iii. Thionin

Figure 1c. Binding isotherms of TriSyl Silicas/Dye Systems.

The initial binding constant, K_i , is the initial slope of the binding isotherm, and thus the average binding strength of a solute molecule by a single monomer unit on an occupied chain. In the u.s.b. model it is equal to the product Kn .

There is a wide variety of methods available for testing whether or not the data from a particular binding system fit the hyperbolic of Eq. 3 and for obtaining the ‘best’ estimates of the parameters K and n .

Whatever the method of testing and fitting chosen, the values K and n obtained should always be checked by plotting the predicted binding isotherm and showing that the experimental data do fit this within the limits of uncertainty. If the fit is not satisfactory, the parameters K and n may be adjusted either until

the optimum fit is obtained, or until it is evident that the data cannot in fact be made to fit this model satisfactorily.

In order to obtain the best values of the binding parameters from the experimental data, Klotz and Langmuir¹⁸ developed linearization methods of Eq. 3.

The Klotz Method

If the isotherm (Eq. 3) is multiplied out and then divided throughout by $C K n r$, this gives^{16,17}

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK} \frac{1}{C} \quad (4)$$

Thus, if this isotherm holds then a plot of $1/r$ vs. $1/C$ will be straight line of slope $1/Kn$, with an ordinate intercept of $1/n$. This is an extremely method of plotting, with the scatter in the r and C values reflected in scatter in the ordinate and abscissa values, respectively. Its limitations are that the intercepts may be small and hence difficult to read off.

Klotz plots of TriSyl silicas/BB 17, BCB, JG B, BG 4, BV 1, BV 3 and T dye-systems are shown in Fig. 2, and binding parameters of TriSyl/BB 17, BCB, JG B, BG 4, BV 1, BV 3 and T dye systems were calculated from the intercepts and slopes of Klotz plots.

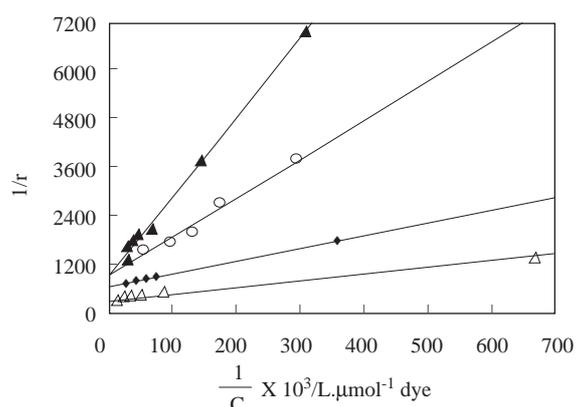


Figure 2a. Klotz plots of TriSyl Silicas/Dye Systems
-▲-; T -○-; BV1 -◆-; BB 12 -△-; JGB

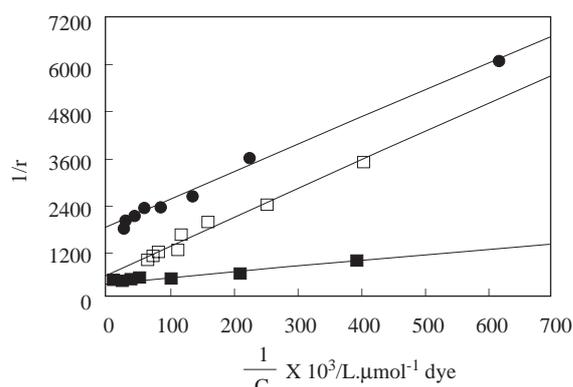


Figure 2b. Klotz plots of TriSyl Silicas/Dye Systems.
-●-; BG 4 -□-; BV3 -■-; BCB

The Langmuir Method

Multiplying the Klotz form of Eq. 3 by C gives¹⁶:

$$\frac{C}{r} = \frac{1}{nK} + \frac{C}{n} \quad (5)$$

so that here a plot of C/r vs. C should be the straight line slope $1/n$, with an ordinate intercept of $1/nK$.

Langmuir plots of TriSyl silicas/BB 9 and BB 17 dye systems are shown in Fig. 3, and binding parameters of TriSyl silicas/BB 9 and BB 17 dye systems were calculated from the intercepts and slopes of Langmuir plots.

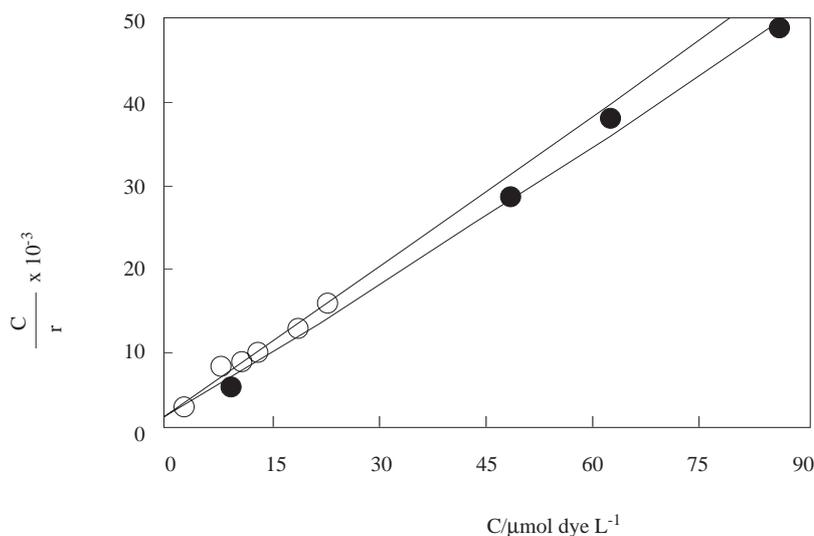


Figure 3. Langmuir plots of TriSyl Silicas/Dye Systems -○-; BB9 -●-; BB17

The derived values of the binding parameters K and n are listed in Table 2 for dyes with TriSyl silicas. The final column contains the derived values of $\hat{\theta}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy θ :

$$\theta = r/n \quad (6)$$

using the value of r at the maximum experimental free dye concentration, and with site-density obtained for the u.s.b. model¹⁴.

Adsorption free energies (ΔG) of hydrogel-dye systems were calculated following equation:

$$\Delta G = -RT \ln K \quad (7)$$

where R, T and K are the universal gas constant, the absolute temperature, and the equilibrium constant of the adsorption process, respectively²⁰.

The values of binding parameters calculated from Klotz or Langmuir binding isotherms and the values of free energy are also given in Table 2.

Table 2. Binding and Thermodynamic Parameters for TriSyl Silicas/Dye Systems

Solution	$K_i/L \text{ mole}^{-1}$	$K/L \text{ mole}^{-1}$	$n \times 10^3$	u	$\hat{\theta}$	$\Delta G/kJ \text{ mole}^{-1}$
Basic Blue 9	1020.45	630481	1.62	617.85	0.97	-33.10
Basic Blue 12	302.22	191157	1.58	632.52	0.87	-30.14
Basic Blue 17	509.79	263286	1.94	516.46	1.00	-30.94
Brilliant Cresyl Blue	717.57	265846	2.70	370.48	0.95	-30.96
Janus Green B	594.13	181754	3.27	305.92	1.00	-30.02
Basic Green 4	137.83	242057	0.57	1756.16	0.96	-30.73
Basic Violet 1	105.56	106628	0.99	1010.16	0.70	-28.70
Basic Violet 3	133.28	69188	1.93	519.12	0.64	-27.63
Thionin	48.85	37112	1.32	759.70	0.76	-26.08

If Table 2 is examined, it will be seen that the values of monolayer coverage of TriSyl silicas by the cationic dyes are increased by the following order:

$$JGB > BCB > BB17 > BV3 > BB9 > BB12 > T > BV1 > BG4$$

On the other hand, if the values of K are examined, it will be seen that the BB 9-TriSyl silica system is the best binding system of all dye-TriSyl systems, i.e., TriSyl silicas were sorbed to BB 9 molecules for the best form of sorption of all dye-TriSyl systems.

The calculated ΔG values of TriSyl silica water-soluble cationic dye binding systems from Eq. 7 are negative, and thus the binding processes of the dyes onto silica gel are spontaneous.

ΔG values are increased by the following order:

$$BB9 > BCB > BB17 > BG4 > BB12 > JGB > BV1 > BV3 > T$$

Finally, influences of mass of TriSyl silicas on dye adsorptions were investigated. Synthetic aqueous solutions of the dyes were prepared in the constant concentrations. TriSyl silicas of increasing mass were transferred into 50 ml of aqueous solutions of the aqueous dye solutions and allowed to equilibrate for two days at 25°C in a water bath.

Percentages of dye removed from solutions were calculated, and these values were plotted versus the mass of TrySyl silicas and are presented in Fig. 4.

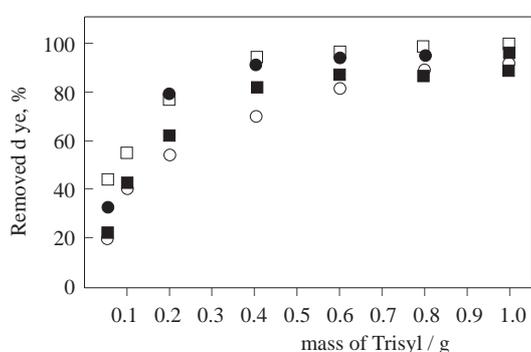


Figure 4a. The variation of percentage of dye removed from solution by mass of TriSyl Silicas. -□-; JGB -●-; BB12 -■-; BV 1 -○-; BG4

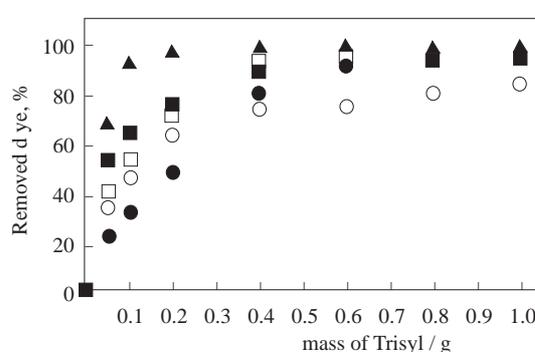


Figure 4b. The variation of percentage of dye removed from solution by mass of TriSyl Silicas. -▲-; BB9 -■-; BV3 -□-; BCB -○-; T -●-; BB17

Figure 4 shows that the percentage of dye removed from solutions initially increased with the increase of the mass of TriSyl silicas, and then reached a constant value. It can be seen that the most suitable mass of TriSyl silicas for the percentage of dye removed from solutions was found to be in the range of 0.7-1.0 g for the dyes in Fig. 4.

Conclusion

The present study offers quantitative information on the binding characteristics of Basic Blue 9, Basic Blue 12, Basic Blue 17, Brilliant Cresyl Blue, Basic Green 4, Janus Green B, Basic Violet 1, Basic Violet 3, and Thionin with TriSyl silicas.

Klotz and Langmuir linearization methods were used in order to examine the binding isotherms. Some binding and thermodynamic parameters were found. Negative ΔG values of TriSyl silica dye binding systems showed the binding processes of the water-soluble cationic dyes onto silica gel to be spontaneous. The most suitable mass of TriSyl silicas for the percentage of dye removed from solutions were found to be in the range of 0.7-1.0 g.

From these adsorption studies, it is seen that silica gel (TriSyl) may be used as an adsorbent for removal of cationic dyes from water, a serious problem in the textile industry.

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