STUDY OF SORPTION OF TRIPHENYLMETHANE DYES ON A MAGNETIC CARRIER BEARING AN IMMOBILIZED COPPER PHTHALOCYANINE DYE

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Magnetite particles bearing covalently immobilized copper phthalocyanine dye ("blue magnetite") were prepared and used for the sorption of triphenylmethane dyes from aqueous solutions. The binding of some triphenylmethane dyes bearing two or three amino groups (basic fuchsin, crystal violet, malachite green) followed the Langmuir adsorption model. The maximum adsorption capacities were calculated. Dyes having no amino group in their molecules exhibited only low adsorption to immobilized copper phthalocyanine. The presence of amino groups in the molecules of triphenylmethane dyes seems to be necessary for their efficient binding on blue magnetite. Generally, efficient sorption of the organic compounds to immobilized copper phthalocyanine may be conditional on a cooperative effect of two parameters, viz. a certain planarity of the sorbate molecule and interaction of the central copper ion of the phthalocyanine molecule with the sorbate amino group or heterocyclic nitrogen atom.

Sorbents prepared by immobilization of copper phthalocyanine dyes on a suitable carrier are known to adsorb selectively polycyclic compounds having three or more fused rings in their molecules. Such compounds are often mutagens and carcinogens, and thus their selective adsorption is useful as a means of extracting this class of chemicals from crude samples such as food, urine and environmental samples. The adsorption takes place in aqueous media and involves the formation of 1 : 1 complexes between the immobilized ligand (i.e., copper phthalocyanine dye) and the polycyclic compound. Desorption can be achieved by elution with organic solvents, most effectively with methanol containing ammonia[1,2].

The main parameter which is assumed to be responsible for the selective binding of polycyclic compounds is the planarity of their molecules. They can form face-to-face hydrophobic complexes with the copper phthalocyanine moiety, which has a large planar surface in the molecule[1]. If the sorbate molecule planarity is the main factor for its specific binding on the immobilized phthalocyanine, some other organic non-polycyclic molecules having planar molecular structure should adsorb on the above mentioned affinity sorbent. Generally, organic molecules with central carbon atoms in the hybridization state *sp*^{2} possess a planar configuration of the three equivalent σ bonds. If the groups bound to this central carbon atom are also planar, there may be a good chance for the specific binding of such molecules on immobilized phthalocyanine.

Triphenylmethane dyes (for general structure see Fig. 1) are an example of such molecules with suggested planarity; of course, this planarity may not be perfect due to the possible interactions of the planar but bulky aromatic rings and of the side chains. The adsorption properties of 7 compounds with the same general structure but differing in the presence of various side chains (see Fig. 1 and Table I) are characterized in this paper.

EXPERIMENTAL

Materials

Reactive copper phthalocyanine dye (Ostazin turquoise V-G; C.I. Reactive Blue 21) was from Spolek pro chemickou a hutni vyrobu, Usti nad Labem, The Czech Republic. Iron(II, III) oxide (magnetite) was obtained from Aldrich, U.S.A.; the diameter of the particles ranged from 1 to 5 μm. Crystal violet (Basic Violet 3; C.I. 42555; m.w. 408.0; purity 75%), basic fuchsin (Basic Red 9; C.I. 42500; m.w. 323.8; purity 75%), aniline blue, water soluble (Water Blue; Methyl Blue; C.I. 42755; m.w. 737.7; purity 75%), aluminon (aurintricarboxylic acid, ammonium salt; C.I. 43810; m.w. 473.4; purity 90%) and common chemicals were from Lachema, The Czech Republic. Malachite green (C.I. 42000; m.w. 419.5; purity 75%) was obtained from Roth, Germany. Chrome azurol S (C.I. 43825; m.w. 605.3; purity 75%) was from Koch-Light Laboratories, England. Rubin S (fuchsin acid; acid fuchsine; C.I. 42685; m.w. 585.5; purity 75%) was obtained from Schering, Germany. 3-Aminopropyltriethoxysilane was from Sigma, U.S.A. Strong permanent magnets of the Ormacon type, used for the separation of magnetic particles, were obtained from Dr Z. Blazek, Department of Magnets, National Research Institute of Materials in Prague, The Czech Republic. Alternatively the magnetic separations were performed using MPC-1 and MPC-6 magnetic separators from Dynal, Norway.

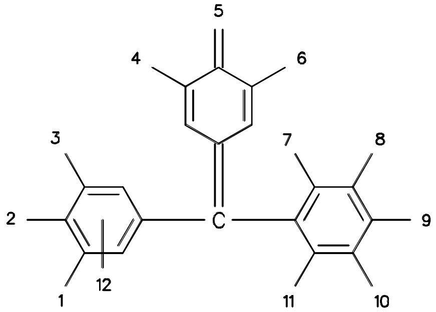

FIG. 1
General structure of the triphenylmethane dyes used. The numbers indicate the presence of the side chains, shown in Table I

Preparation of Magnetic Sorbent (“Blue Magnetite”)

The procedure was as described previously[3]. Iron(II, III) oxide (10 g) was suspended in 5% nitric acid and boiled in a closed vessel at 100 °C for 60 min. After thorough washing with distilled water, 40 ml of a 10% aqueous solution of 3-aminopropyltriethoxysilane (pH 4.0; adjusted with HCl) were added to the sedimented magnetite. The suspension was stirred on a water bath at 80 °C for 4 h, after which the silanized magnetite was thoroughly washed with water.

The silanized magnetite was suspended in 200 ml of water and the suspension was mixed with 4 g of Ostazin turquoise V-G (C.I. Reactive Blue 21) and 12 g of sodium chloride. The suspension was warmed to 70 °C, and in 15 min 10 g of anhydrous sodium carbonate were added. The suspension was stirred at 70 °C for 4 h, after which the mixture was left overnight at ambient temperature without mixing. The blue magnetite particles were thoroughly washed with water and the remaining free dye was removed by extraction with methanol in a Soxhlet apparatus. The extracted particles were repeatedly washed with a methanol–concentrated NH_4OH mixture (50 : 1; v/v) and with dimethyl sulfoxide until only faint blue washings were obtained. The washed blue magnetite particles were stored in water at 4 °C. The dry weight of 1 ml of the settled blue magnetite was 322 mg.

TABLE I

Side chains and counter ions of the triphenylmethane dyes tested. For general formula, see Fig. 1

Position	Side chains						
	aluminon	aniline blue	basic fuchsin	chrome azurol S	crystal violet	malachite green	rubin S
1	H	H	H	CH_3	H	H	CH_3
2	OH	NH_2	NH_2	OH	$N(CH_3)_2$	H	NH_2
3	$COONH_4$	CH_3	H	COONa	H	H	SO_3Na
4	H	H	H	CH_3	H	H	H
5	O	N-Phe-SO_3H	$^+NH_2$	O	$^+N(CH_3)_2$	$^+N(CH_3)_2$	NH
6	$COONH_4$	H	H	COONa	H	H	SO_3Na
7	H	H	H	Cl	H	H	H
8	H	H	H	SO_3Na	H	H	SO_3H
9	OH	NH-Phe-SO_3Na	NH_2	H	$N(CH_3)_2$	$N(CH_3)_2$	NH_2
10	$COONH_4$	H	H	H	H	H	H
11	H	H	H	Cl	H	H	H
12	–	SO_3Na	–	–	–	–	–
	counter ions						
	–	–	Cl^-	–	Cl^-	$^-OOCCOOH$	–

Determination of Sorption Capacity of “Blue Magnetite”

The suspensions of blue magnetite (200 μl; the settled volume of the sorbent was 50 μl) in 15 ml polystyrene test tubes were diluted with 8.8 ml of water, and 0.01 – 1.0 ml portions of aqueous stock solutions (1 – 5 mg ml^{-1}) of the triphenylmethane dyes were added and the total volume of the suspension was made up to 10.0 ml with water. Aqueous solutions of the dyes for the construction of the calibration curves were prepared likewise, only 200 μl of water were used instead of the same volume of the blue magnetite suspension. The suspensions were mixed for 2 h at 20 °C, and the blue magnetite particles were separated from the suspension using a magnetic separator or a permanent magnet held on the test-tube wall and the absorbances of the clear supernatants were measured. The concentration of the free (unbound) dye in supernatant (C_{eq}) was determined from the calibration curve, and the amount of dye bound to the unit volume of sorbent (q_{eq}) was calculated by difference, using the following formula (Eq. (*1*)):

$$q_{eq} = (D_{tot} - 10\, C_{eq})/50 \quad (\mu g\ mm^{-3} \text{ or } mg\ cm^{-3}) , \qquad (1)$$

where D_{tot} is the total amount of dye used in an experiment.

Other Procedures

The amount of copper phthalocyanine bound to magnetic particles was estimated, after mineralization with concentrated nitric acid, from elemental analysis for copper using a PU 7450 ICP spectrometer (Pye-Unicam, England).

RESULTS

Silanization of the magnetite particles and subsequent immobilization of the reactive copper phthalocyanine dye led to the formation of a magnetically responsive sorbent with affinity for the majority of the organic triphenylmethane compounds tested. The copper phthalocyanine content of the blue magnetite was ca 71 μmol per gram of dry

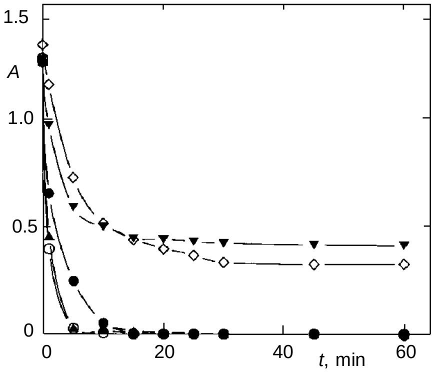

FIG. 2
Time dependence of the adsorption of the tested dyes on blue magnetite. For symbols see Fig. 3. *A* Absorbance of supernatants, *t* time of adsorption

sorbent. The sorbent particles can be easily separated from the solutions or suspensions using permanent magnets or commercially available magnetic separators.

Preliminary experiments indicated that the sorption of the dyes reached equilibrium in approximately 30 min (see Fig. 2). In the subsequent experiments, the sorption of the dyes was performed for two hours.

Equilibrium sorption isotherms for unbuffered aqueous solutions of the triphenylmethane dyes (for structures, see Fig. 1 and Table I; blue magnetite used as sorbent) are shown in Fig. 3. Sorption isotherms represent the equilibrium distribution of the dye molecules between the aqueous and solid phases as the dye concentration is increased. The isotherms were evaluated in terms of the classification system of adsorption isotherms suggested by Giles et al.[4]. The binding of the dye to the surface of blue magnetite was then evaluated in terms of the Freundlich and Langmuir isotherms using the following linearized forms of the equations (*2*) and (*3*).

Freundlich isotherm

$$\log q_{\mathrm{eq}} = \log k + \frac{1}{n} \log C_{\mathrm{eq}} \qquad (2)$$

Langmuir isotherm

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{eq}}} = \frac{1}{bQ} + \frac{C_{\mathrm{eq}}}{Q} \; , \qquad (3)$$

where b is the constant of the Langmuir isotherm ($\mathrm{dm^3\,mg^{-1}}$), C_{eq} is equilibrium liquid-phase concentration of the unadsorbed (free) dye ($\mathrm{mg\,dm^{-3}}$), q_{eq} is equilibrium solid-phase concentration of the adsorbed dye (in $\mathrm{mg\,cm^{-3}}$ for calculations based on the

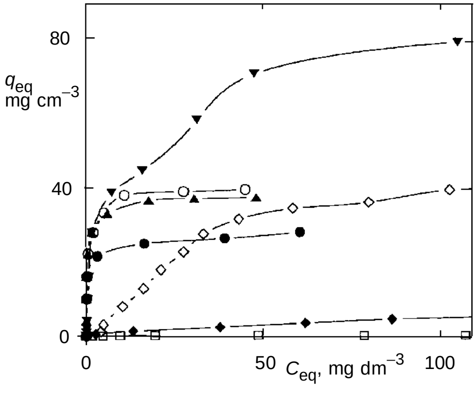

FIG. 3
Equilibrium sorption isotherms of aluminon (❐), aniline blue (✧), basic fuchsin (▲), chrome azurol S (◆), crystal violet (●), malachite green (❍) and rubin S (▼) using blue magnetite as sorbent. C_{eq} Equilibrium liquid-phase concentration of the unadsorbed (free) dye ($\mathrm{mg\,dm^{-3}}$), q_{eq} equilibrium solid-phase concentration of the adsorbed dye (dye uptake) ($\mathrm{mg\,cm^{-3}}$)

settled volume of the magnetic sorbent, or in mg g^{-1} for calculations based on dry weight of the sorbent), k is the constant of the Freundlich isotherm and Q is maximum adsorption capacity of the sorbent (in mg cm^{-3} for calculations based on the settled volume of the magnetic sorbent, or in mg g^{-1} for calculations based on dry weight of the sorbent).

The isotherms of dyes which exhibit strong sorption (dyes in the diamino and triamino groups) were evaluated in terms of the system of Giles et al.[4]. Crystal violet, basic fuchsin and malachite green followed the typical Langmuir adsorption pattern (class L2), as also indicated by the linear transformation (Fig. 4), whereas the isotherm for rubin S belongs to class L4 and that for aniline blue to class C, where the Langmuir linear transformation showed deviations from the ideal behaviour (Fig. 4). Triphenylmethane dyes belonging to the hydroxy group (chrome azurol S and aluminon) exhibited a very low adsorption to the immobilized copper phthalocyanine dye in comparison with the dyes of the diamino group (malachite green) and triamino group (aniline blue, basic fuchsin, crystal violet and rubin S). Both chrome azurol S and aluminon followed the Freundlich model but not the Langmuir model (data not shown). While the Langmuir model involves several assumptions[5] (sorbate is chemically adsorbed at a fixed number of well-defined sites; each site can hold one sorbate molecule; all sites are energetically equivalent; there is no interaction between molecules adsorbed on neighbouring sites), the Freundlich equation applies to heterogeneous surface adsorption.

Linear transformation of the Langmuir equation allows the maximum adsorption capacities Q to be determined (see Table II). The Q values were only calculated for dyes in the L2 class (crystal violet, basic fuchsin and malachite green), whereas for the remaining two amino dyes (rubin S, aniline blue) they were estimated from the adsorption isotherms. Due to the fact that the dyes used were no pure substances, the corrected

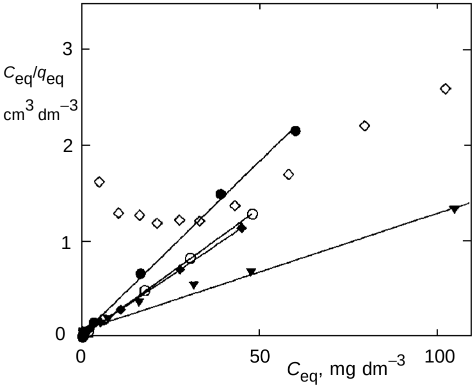

FIG. 4
Langmuir transformation of equilibrium sorption isotherms for aniline blue, basic fuchsin, crystal violet, malachite green and rubin S (blue magnetite used as sorbent). The symbols and captions are the same as in Fig. 3

maximum adsorption capacities Q' (in mg cm^{-3} or mg g^{-1}) and Q'' (in μmol cm^{-3} or μmol g^{-1}) were calculated using the known degree of purity of the dyes.

To find whether the sorption of the dyes was caused by the presence of the immobilized copper phthalocyanine dye or if sorption on the silanized magnetite was involved the sorption experiments were carried out with the silanized magnetite only. As Fig. 5

TABLE II

Maximum adsorption capacities, Q, and Langmuir constants, b, calculated from the Langmuir equation (*3*). Blue magnetite was used as a specific sorbent. Q' and Q'' are the maximum adsorption capacities calculated for the pure dyes. The values in upper rows are calculated using the settled volume of the magnetic sorbent; the values in lower rows (in parentheses) are calculated using the dry weight of the sorbent

Dye	Q mg cm^{-3} (mg g^{-1})	Q' mg cm^{-3} (mg g^{-1})	Q'' μmol cm^{-3} (μmol g^{-1})	b dm^3 mg^{-1} (dm^3 mg^{-1})
Aniline blue[a]	45 (139.7)	34 (105.6)	45.7 (141.9)	–
Basic fuchsin	37.6 (116.8)	28.2 (87.6)	87.0 (270.2)	2.41 (2.41)
Crystal violet	27.7 (86.0)	20.8 (64.6)	51.0 (158.4)	1.20 (1.20)
Malachite green	40.0 (124.2)	30.0 (93.2)	71.6 (222.4)	1.40 (1.40)
Rubin S[a]	82 (254.6)	61.5 (191.0)	105.0 (326.1)	–

[a] Q was estimated from the adsorption isotherm.

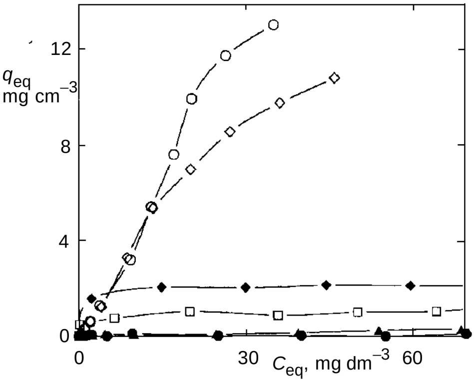

FIG. 5

Equilibrium sorption isotherms of aluminon, aniline blue, basic fuchsin, chrome azurol S, crystal violet, malachite green and rubin S using silanized magnetite as sorbent. The symbols and captions are the same as in Fig. 3

demonstrates, only aniline blue and malachite green exhibited some non-specific sorption on the plain silanized magnetite; this sorption was substantially lower than the sorption on blue magnetite. Basic fuchsin, crystal violet, rubin S, aluminon and chrome azurol S, on the other hand, exhibited almost no sorption on silanized magnetite.

Among factors that can influence the sorption of the dyes examined is the presence of ionic groups both in the phthalocyanine molecules (sulfonate groups) and in the triphenylmethane dyes molecules (see Table I). To eliminate possible ionic interactions, the sorption of the dyes was also measured in the presence of 0.2 M sodium chloride: it was identical with the sorption in the absence of the salt. This gives evidence that ionic interactions contribute little to the observed adsorption.

DISCUSSION

The results show that the magnetic sorbent bearing immobilized copper phthalocyanine dye (blue magnetite) can adsorb a majority of the triphenylmethane dyes tested. All of the dyes adsorbing strongly on blue magnetite possess two or three amino groups, whereas the dyes exhibiting a very low adsorption (aluminon and chrome azurol S) belong to the hydroxy group of triphenylmethane dyes, having no amino groups in their molecules.

One of the possible explanations of the observed behaviour is that the triphenylmethane dye molecules are not perfectly planar, due to the steric hindrances of the bulk phenyl groups and of the side chains. The sorption of such molecules on the immobilized copper phthalocyanine dye can only be successful if there are some other interactions stabilizing the phthalocyanine–sorbate molecular complex. It is known that copper ion, which is an integral part of the copper phthalocyanine dye, can easily interact with amino groups or with nitrogen atoms in heterocyclic compounds, forming complex compounds[6]. In the phthalocyanine molecule, the central copper ion binds to four nitrogen atoms of the pyrrole rings. Presumably, other nitrogen atoms with free electron pairs in the sorbate molecules can interact with the copper ion as well. This phenomenon may be responsible for the observed binding of diamino and triamino derivatives of the dyes studied.

The presence of amino groups in the organic molecule, however, is no guarantee of sorption of the molecule on the immobilized copper phthalocyanine dye. It has been shown recently[3] that congo red, possessing two amino groups (but no planar structure) adsorbs on blue magnetite to a very low degree.

Probably, efficient sorption of the organic compounds to the immobilized copper phthalocyanine is conditional on a joint effect of two parameters, viz. a certain planarity of the molecule and interaction of the central copper ion of the phthalocyanine dye with a sorbate amino group or nitrogen atom in a heterocycle.

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