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Ivo Šafařík[a]; Mirka Šafaříková[a]
[a] LABORATORY OF BIOCHEMISTRY AND BIOTECHNOLOGY, INSTITUTE OF LANDSCAPE, ČESKÉ, BUDĚJOVICE, CZECH REPUBLIC

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TECHNICAL NOTE

Copper Phthalocyanine Dye Immobilized on Magnetite Particles: An Efficient Adsorbent for Rapid Removal of Polycyclic Aromatic Compounds from Water Solutions and Suspensions

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IVO ŠAFAŘÍK* and MIRKA ŠAFAŘÍKOVÁ
LABORATORY OF BIOCHEMISTRY AND BIOTECHNOLOGY
INSTITUTE OF LANDSCAPE ECOLOGY
BRANIŠOVSKÁ 31, 370 05 ČESKÉ BUDĚJOVICE, CZECH REPUBLIC

ABSTRACT

Magnetite particles bearing covalently immobilized copper phthalocyanine dye ("blue magnetite") were prepared and used for the isolation and/or removal of polycyclic dyes from water solutions and suspensions. Binding of these polycyclic dyes occurs by a chemical, equilibrated, and saturatable mechanism, following the Langmuir adsorption model. Nonspecific adsorption of dyes having nonplanar molecular structure was low. The values of maximum adsorption capacity were calculated. The bound dyes were only partially eluted from the adsorbent with methanol and methanol–concentrated ammonia solution (50/1, v/v).

Key Words. Magnetic particles; Magnetite; Iron (II,III) oxide; Phthalocyanine dye; Polycyclic compounds; Blue magnetite

INTRODUCTION

It has been shown recently that phthalocyanine dyes immobilized on a proper carrier can effectively and specifically adsorb polycyclic compounds having three or more fused aromatic rings in their molecules. These compounds are commonly planar in their molecular form and they

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* To whom correspondence should be addressed. FAX: +42038 40198. E-mail: safarik@dale.uek.cas.cz

can probably form face-to-face hydrophobic complexes with copper phthalocyanine moiety, which has a large planar surface in the molecule (1).

Separation of polycyclic aromatic compounds from water solutions and/or suspensions and from clinical samples can be simplified using magnetic adsorbents carrying immobilized phthalocyanine dye (2, 3). Recently a chitosan-based adsorbent ("magnetic blue chitosan") has been prepared; this adsorbent was used for effective adsorption of water-soluble polycyclic dyes. The chitosan matrix of the adsorbent, however, was responsible for the nonspecific binding of congo red, which is a typical representant of direct dyes with a linear molecular structure (3).

In this work, copper phthalocyanine dye has been immobilized on silanized magnetite particles. Due to the absence of a polysaccharide matrix, the possibility of nonspecific interactions is strongly reduced. This magnetic adsorbent (called "blue magnetite" throughout this paper) can be directly used for the removal of polycyclic compounds from water solutions and suspensions without any pretreatment of the analyzed sample.

EXPERIMENTAL

Materials

Reactive copper phthalocyanine dye (Ostazin turquoise V-G; C.I. Reactive Blue 21) was from Spolek pro chemickou a hutní výrobu, Ústí nad Labem, Czech Republic. Iron(II,III) oxide (magnetite) was obtained from Aldrich, USA; the diameter of the particles ranged from 1 to 5 μm. Congo red (declared purity 50%) and Safranin O (declared purity 96%) were from Sigma, USA. Acridine Orange (assumed purity 75%) was from Merck, Germany. Neutral Red (assumed purity 75%), Thionine (assumed purity 75%), Methylene Blue (assumed purity 75%), and common chemicals were from Lachema, Czech Republic. 3-Aminopropyltriethoxysilane was from Sigma, USA. Magnetic separations were performed using magnetic separators MPC-1 and MPC-6 from Dynal, Norway.

Preparation of Magnetic Adsorbent ("blue magnetite")

Iron(II,III) oxide (10 g) was suspended in 5% nitric acid and boiled in a closed vessel at 100°C for 60 minutes. After thorough washing with water, 40 mL of a 10% water solution of 3-aminopropyltriethoxysilane (pH 4.0; adjusted with HCl) was added to the sedimented magnetite. The suspension was mixed on a water bath at 80°C for 4 hours. Then the silanized magnetite was thoroughly washed with water. The dry weight of 1 mL of the settled silanized magnetite was 281 mg.

The silanized magnetite was suspended in 200 ml of water, and the suspension was mixed with 4 g of Ostazin turquoise V-G and 12 g of sodium chloride. The suspension was warmed to 70°C, and 15 minutes later 10 g of anhydrous sodium carbonate was added. The suspension was stirred at 70°C for 4 hours and then the mixture was left overnight at ambient temperature without mixing. The blue magnetite particles were thoroughly washed with water, and the remaining free color was removed by extraction with methanol in a Soxhlet apparatus. The extracted particles were then repeatedly washed with 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; the copper phthalocyanine content was ca. 71 μmol/g of dry adsorbent (measured, after mineralization with concentrated nitric acid, from elemental analysis for copper with ICP spectrometry).

Determination of Adsorption Capacity of "Blue Magnetite"

To the suspensions of blue magnetite (200 μL; the settled volume of the adsorbent was 50 μL) in 15-ml polystyrene test tubes, 8.8 mL of water was added. Then 0.01–1.0 mL portions of stock water solutions (1–5 mg/mL) of tested polycyclic dyes were added, and the total volume of the suspension was made up to 10.0 mL with water. In the same manner, water solutions of the tested dyes, used for the construction of the calibration curves, were prepared; instead of 200 μL of blue magnetite suspension, 200 μL of water was used. The suspensions were mixed for 2 hours at 20°C. Then the blue magnetite particles were separated from the suspension using a magnetic separator, and the clear supernatants were used for the measurement of absorbances. The concentration of free (unbound) dye in the supernatant (C_{eq}) was determined from the calibration curve, and the amount of dye bound to the unit volume of adsorbent (q_{eq}) was calculated by difference, using Eq. (1):

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

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

Elution of Bound Dyes

To the suspensions of blue magnetite (200 μL; the settled volume of the adsorbent was 50 μL) in 15-mL polystyrene test tubes, 1 mL of water solutions of the tested dyes (1 mg/mL) were added. After a 2-hour incubation period the dye solution was poured off and the sorbent was washed six times with 2 mL of water. The solutions were combined, and the concentration and the total amount (D_{nb}) of nonbound dye were calculated from the calibration curve. An appropriate eluent solution (5 mL) was then added to the blue magnetite, and after 20 minutes of mixing the solution was poured off. Alternatively, the elution was performed for 14 hours. The concentration and the total amount of released dye (D_{rel}) was calculated from the calibration curve (the dye tested and the eluent solution were used for its preparation). The elution efficiency (E), expressed as a percentage, was calculated from the amounts of bound and released dye according to Eq. (2):

$$E = \frac{100D_{rel}}{D_{tot} - D_{nb}} \, [\%] \qquad (2)$$

RESULTS

The prepared adsorbent (blue magnetite) easily adsorbed polycyclic aromatic compounds with various structures (acridine orange, Neutral Red, Thionine, Methylene Blue, and Safranin O; for structures see Fig. 1); on the contrary, compounds not having the planar structure [e.g., Congo red, which previously strongly adsorbed nonspecifically on magnetic blue chitosan (3)] adsorbed to the blue magnetite to a substantially lower degree. The time dependence of the adsorption of the tested dyes on the blue magnetite showed that equilibrium can be reached in approximately 30 minutes.

Adsorption of the organic compounds tested by blue magnetite was performed in distilled water with no pH control. Equilibrium adsorption isotherms are shown in Fig. 2. These isotherms follow the typical Langmuir adsorption pattern. The isotherms were evaluated according to a classification system of solution adsorption isotherms described by Giles et al. (4). The isotherms belong to Class L2, as also shown by the linear transformation of the data used for the construction of adsorption isotherms (data not shown). The binding of these polycyclic dyes occurs by a chemical, equilibrated, and saturatable mechanism.

The maximum adsorption capacities Q (number of moles or grams of dye adsorbed per unit of sorbent and forming a continuous monolayer on the sorbent surface) were calculated using the known purities of the dyes; they are summarized in Table 1.

To distinguish whether the adsorption of the dyes was caused by the presence of the immobilized phthalocyanine dye or whether adsorption on the silanized magnetite took place, the adsorption experiments were carried out with the silanized magnetite only. Only Congo red exhibited some nonspecific adsorption on the plain silanized magnetite; this adsorp-

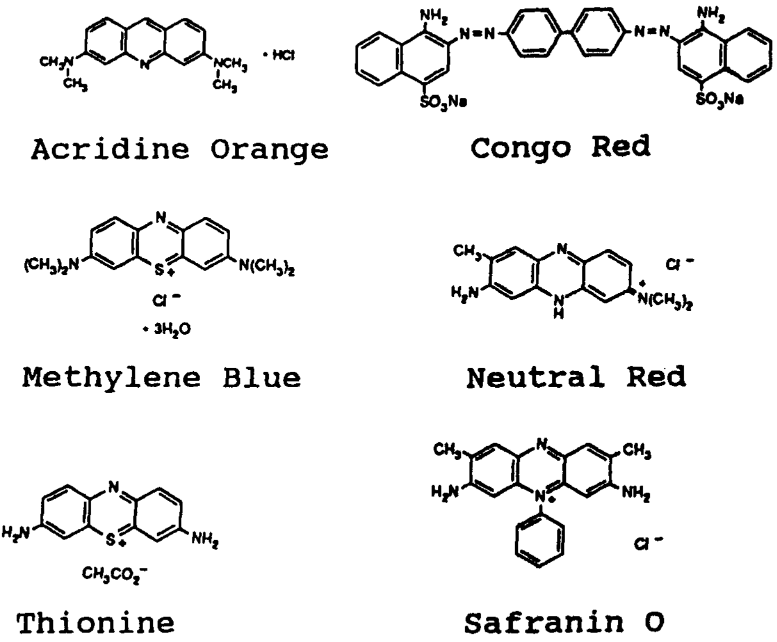

FIG. 1 Structures of dyes used.

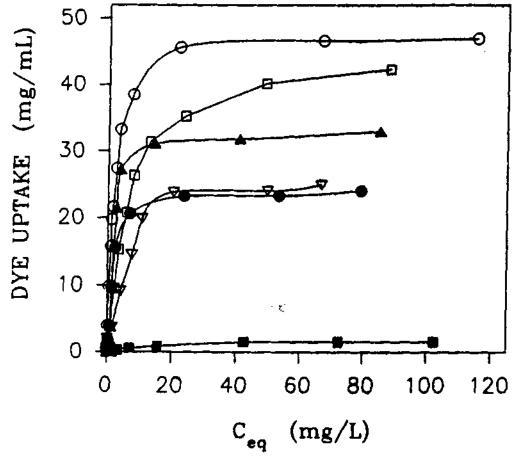

FIG. 2 Equilibrium adsorption isotherms of acridine orange (○), Congo red (■), Methylene Blue (▲), Neutral Red (●), Safranin O (▽), and Thionine (□) using blue magnetite as the adsorbent. The uncorrected dye concentration values were used. C_{eq} = equilibrium liquid-phase concentration of the unadsorbed (free) dye (mg·dm^{-3}). Dye uptake = equilibrium solid-phase concentration of the adsorbed dye (mg·cm^{-3}).

TABLE 1

Maximum Adsorption Capacities of the Dyes Tested (Q and Q') and Langmuir Constants (b), Calculated from the Langmuir Equation Using Known Dye Purity. Blue Magnetite Was Used as the Adsorbent. The Values in the Lines without Parentheses Were Calculated Using the Settled Volume of the Magnetic Adsorbent; The Values in Parentheses Were Calculated Using the Dry Weight of the Adsorbent

Dye	Q, mg/mL (mg/g)	Q', μmol/mL (μmol/g)	b, L/mg (L/mg)
Acridine orange	33.95	112.5	0.496
	(105.4)	(349.4)	(0.496)
Methylene Blue	25.14	78.59	0.654
	(78.08)	(244.1)	(0.654)
Neutral Red	17.77	61.54	0.414
	(55.19)	(191.1)	(0.414)
Safranin O	24.32	69.33	0.606
	(75.54)	(215.3)	(0.606)
Thionine	34.26	123.1	0.148
	(106.4)	(382.3)	(0.148)
Congo red	0.903	1.296	0.069
	(2.805)	(4.025)	(0.069)

tion also followed the Langmuir mechanism (data not shown). On the contrary, polycyclic dyes acridine orange, Neutral Red, Thionine, Methylene Blue, and Safranine O exhibited almost no adsorption. It is interesting that nonspecific adsorption of Congo red on silanized magnetite is substantially higher (Q = 3.46 mg/mL) than adsorption on blue magnetite (Q = 0.90 mg/mL); ionic interactions between negatively charged Congo red and silanized magnetite are probably responsible for this behavior.

One of the factors which can influence the adsorption of the studied dyes is the presence of ionic groups both in the phthalocyanine molecule (sulfonate groups) and in the polycyclic dyes molecules (see Fig. 1). To eliminate possible ionic interactions, the adsorption of the tested dyes in the presence of 0.2 M sodium chloride was measured. It was observed that the adsorption of the dyes on blue magnetite was practically the same both in the absence and in the presence of sodium chloride. Also, small changes of pH of the dye solutions did not cause substantial changes in the binding of the tested dyes. This means that ionic interactions contribute little to the observed adsorption.

Elution of the adsorbed polycyclic compounds from the immobilized phthalocyanine is usually performed with methanol and with methanol-containing concentrated ammonia solution (50/1, v/v). The results of the

TABLE 2

Efficiency of Eluting Solvents. The Elution Time Was 20 Minutes (numbers without parentheses) and 14 Hours (numbers in parentheses)

Dye	Efficiency of elution (%)	
	CH_3OH	CH_3OH-NH_4OH (50:1, v/v)
Acridine orange	21.3 (58.8)	33.6 (71.7)
Methylene Blue	20.8 (41.7)	18.6 (45.8)
Neutral Red	35.6 (89.4)	36.3 (46.7)
Safranin O	28.0 (64.5)	17.9 (43.0)
Thionine	15.1 (32.9)	26.8 (46.4)
Congo red	32.7 (65.6)	39.6 (47.8)

elution experiments (time of elution was 20 minutes or 14 hours) are shown in Table 2. During the prolonged elution, substantial higher amount of dyes could be recovered. Regenerated adsorbents can be reused for binding of the dyes. However, in the case of possible analytical applications, it is preferable to use a new adsorbent for each adsorption.

DISCUSSION

An efficient adsorbent for the selective separation of polycyclic aromatic compounds has been prepared by immobilization of a phthalocyanine dye on the surface of silanized magnetite. The magnetic behavior of the adsorbent enables rapid and efficient removal of the blue magnetite, not only from solutions but also from suspensions. This property is very useful because sorption of the polycyclic aromatic compounds can be performed directly in unprocessed samples, such as wastewater, soil suspensions, mud, etc., containing suspended solids.

The direct immobilization of a phthalocyanine dye on modified magnetite particles improved the properties of the blue magnetite in comparison with the magnetic blue chitosan described previously (3). First, an increase of the selectivity of the new adsorbent was found. While Congo red, a typical example of direct dyes, strongly interacts with a polysaccharide matrix of the magnetic blue chitosan prepared and tested previously (3), the interaction of this dye with blue magnetite is substantially lower, especially in comparison with adsorption of the target polycyclic dyes. Second, the adsorption capacity of blue magnetite is much higher in comparison with magnetic blue chitosan, probably due to the higher surface area of magnetite particles.

The elution of the bound dyes with the two tested elution systems was relatively low, especially for short elution times. In future experiments we will try to modify the elution conditions in order to increase the elution yield.

Further experiments with the adsorption of organic planar molecules on blue magnetite are now in progress.

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