SORPTION OF WATER SOLUBLE ORGANIC DYES ON MAGNETIC POLY(OXY-2,6-DIMETHYL-1,4-PHENYLENE)

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Magnetic composite based on poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP) was prepared by melting the polymer with ε-caprolactam in a presence of fine magnetite particles. Magnetic PODMP was used for sorption of water soluble organic compounds (dyes belonging to triphenylmethane, heteropolycyclic and azo dye groups) from water solutions. There were considerable differences in the binding of the dyes tested. In general, heteropolycyclic dyes exhibited the lowest sorption.

Adsorption is often used as a method of treating aqueous solutions to remove dissolved contaminating organic compounds. Various sorbents are used, most conventional adsorption system being activated carbon[1]. To treat water suspensions containing solid particles batch systems are usually used. Application of magnetic sorbent particles can markedly simplify the manipulation with the sorbent used. Magnetic particles can be easily concentrated and removed from the system using an appropriate magnetic separator.

Various magnetic particles for waste water treatment have been prepared recently[2]. Magnetic ion-exchange microresins or magnetic polymers devoid of functional groups can be prepared in three main forms by incorporating ferromagnetic particles (usually iron oxides magnetite or maghemite) within synthetic polymer beads. The polymers are insolubilized by cross-linking, and may possess a diverse range of functional groups. The homogeneous resins contain magnetic material evenly distributed throughout the resin network. The composite format resins are prepared by placing the active polymer as small particles (1–5 μm in size) plus the magnetic material inside an inert but permeable matrix such as cross-linked poly(vinyl alcohol). Heterogenous resins have a shell structure and are prepared by grafting active polymeric chains onto a magnetic polymeric core that is formed by including magnetic particles within an inert polymer matrix. The above mentioned magnetic particles have been used for decoloration of pulp mill effluent[3], adsorption of oil spills from waters[4] or removal of heavy metal ions[5]. Magnetic chitosan particles bearing copper phthalocyanine dye have been used for selective recovery of polycyclic aromatic compounds[6].

Not only polymer particles, but also unmodified magnetite can be used in waste water treatment, due to its ion-exchange and flocculating properties[7,8].

Organic compounds represent an important group of environmental contaminants. For their removal various magnetic sorbents have been tested. In this study, a linear hydrophobic polymer poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP) has been selected as a possible candidate for the efficient sorbent for the removal of this class of compounds. This polymer is similar to Tenax TA (poly(oxy-2,6-diphenyl-1,4-phenylene)), which is used as a column packing in gas chromatography for separation of amines, alcohols, aldehydes, ketones and aromatic compounds[9]. PODMP is produced commercially, thus being relatively cheap material. It can be melted easily; melting in the presence of ferromagnetic material produces magnetic polymer composite the ability of which to adsorb organic dyes from water solutions has been tested.

EXPERIMENTAL

Materials

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP) and ε-caprolactam were obtained from Dr B. Veruovic, Department of Polymers, Prague Institute of Chemical Technology, Czech Republic. PODMP is a synthetic linear polymer with the structure shown in Fig. 1. The weight-average molecular weight of the polymer used[10] was approximately 17 000. Iron(II,III) oxide (magnetite) was obtained from Aldrich, U.S.A.; the diameter of the particles ranged from 1 to 5 μm. Congo red (Direct Red 28; C.I. 22120; m.w. 696.7; declared purity 50%), safranine O (C.I. 50240; m.w. 350.8; declared purity 96%) and Bismarck brown Y (Basic Brown 1; C.I. 21000; m.w. 419.3; declared purity 50%) were from Sigma, U.S.A. Thionin (Lauth's Violet; C.I. 52000; m.w. 278.3; assumed purity 75%), methylene blue (C.I. 52015; m.w. 319.9; assumed purity 75%), crystal violet (Basic Violet 3; C.I. 42555; m.w. 408.0; assumed purity 75%), aniline blue, water soluble (Water Blue; Methyl Blue; C.I. 42755; m.w. 737.7; assumed purity 75%) and common chemicals were from Lachema, Czech Republic. Rubin S (Fuchsin Acid; Acid Fuchsin; C.I. 42685; m.w. 585.5; assumed purity 75%) was obtained from Schering, Germany. Strong permanent magnets of the Ormakon type, used for the separation of magnetic PODMP particles, were obtained from Dr Z. Blazek, Department of Magnets, National Research Institute of Materials, Prague, Czech Republic. Alternatively the magnetic separations were performed using magnetic concentrators MPC-1 and MPC-6 from Dynal, Norway.

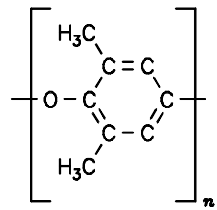


FIG. 1
Chemical structure of poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP)

Preparation of Magnetic PODMP

PODMP (10 g) was mixed with ε-caprolactam (50 g) and powdered magnetite (10 g) in a glass beaker. The mixture was heated (in a fume hood) on a hot plate under mixing. After complete dissolution of PODMP in the melted ε-caprolactam (approximately at 170–180 °C) the suspension was allowed to cool under mixing. The black solid material was milled in a coffee mill with rotating knives to obtain small particles (0.01–0.25 mm in diameter); they were thoroughly washed with methanol in a Soxhlet apparatus in order to extract ε-caprolactam. After methanol extraction the magnetic PODMP particles were gradually transferred from methanol to water. The dry weight of 1 ml of the settled magnetic PODMP was 212 mg. The sorbent particles can be easily separated from the solutions or suspensions using permanent magnets or commercially available magnetic concentrators.

Determination of Sorption Capacity of Magnetic PODMP

To the suspensions of magnetic PODMP (200 μl; the settled volume of the sorbent was 50 μl) in 15-ml polystyrene test tubes 8.8 ml of water were added. Then 0.01–1.0 ml portions of stock water solutions (1–5 mg ml^{-1}) of the dyes tested 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 magnetic PODMP suspension 200 μl of water were used. The suspensions were mixed for 4 h at 20 °C. Then the magnetic PODMP particles were separated from the suspension using a magnetic concentrator or a permanent magnet held on the test-tube wall 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 on the unit volume of the sorbent (q_{eq}) was calculated by difference, using the following formula:

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

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

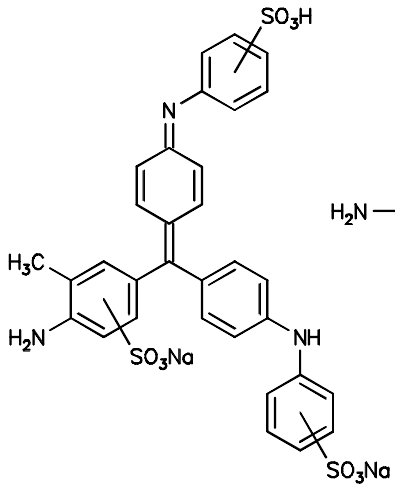
Elution of Bound Dyes

To the suspensions of magnetic PODMP (200 μl; the settled volume of the sorbent was 50 μl) in 15-ml polystyrene test tubes 1 ml of water solutions of the tested dyes (1 mg ml^{-1}) were added. After 4 h incubation period the dye solutions were poured off completely; the concentration and the total amount (D_{nb}) of non-bound dye were calculated from the calibration curve. The eluent solution tested (5 ml) was then added to the magnetic PODMP and after 15 min mixing the solution was poured off. The concentration and the total amount of the released dye (D_{rel}) were calculated from the calibration curve (the dye tested and the eluent solution were used for its preparation). The elution efficiency (E), expressed in percentage, was calculated from the amounts of bound and released dye according to the following equation:

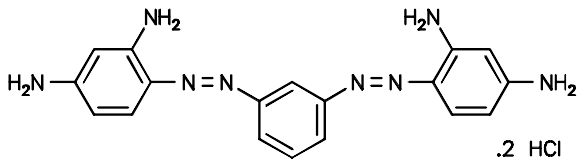
$$E = \frac{100\ D_{rel}}{D_{tot} - D_{nb}}\ \% \ .$$

RESULTS

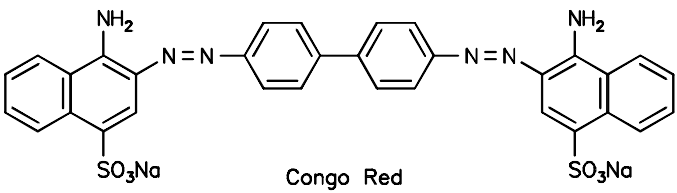
Water soluble organic dyes belonging to triphenylmethane, heteropolycyclic and azo-dye groups were used as model compounds in adsorption experiments; for their structures see Fig. 2. It was shown in preliminary experiments that the sorption of the tested



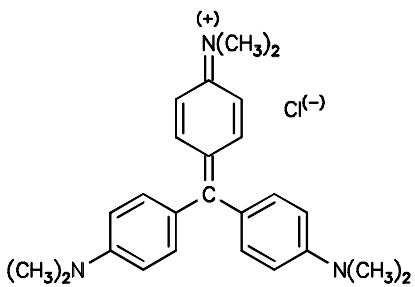
Aniline Blue



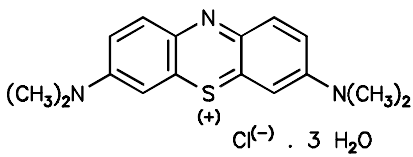
Bismarck Brown Y



Congo Red



Crystal Violet



Methylene Blue

FIG.2
Chemical structures of the dyes tested

dyes reached equilibrium in approximately 60–90 min (see Fig. 3). In the following experiments, the sorption of the dyes took place for 4 h.

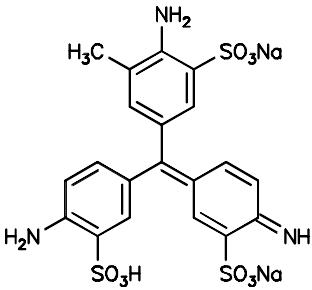
Equilibrium sorption isotherms for the unbuffered water solutions of the dyes tested and magnetic PODMP as sorbent are shown in Fig. 4. As can be seen, the dyes tested can be divided into two groups according to their sorption to the magnetic PODMP. Aniline blue, Bismarck brown Y, congo red and crystal violet exhibited better sorption than methylene blue, rubin S, safranine O and thionin.

The binding of the dyes to the surface of magnetic PODMP was considered in terms of the Freundlich and Langmuir isotherms, the following linearized forms being used:

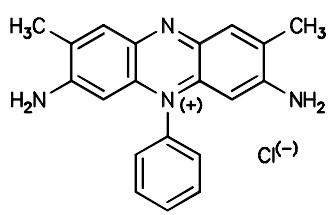
Freundlich isotherm: $$\log q_{eq} = \log k + \frac{1}{n} \log C_{eq}$$

Langmuir isotherm: $$\frac{C_{eq}}{q_{eq}} = \frac{1}{bQ} + \frac{C_{eq}}{Q} \quad ,$$

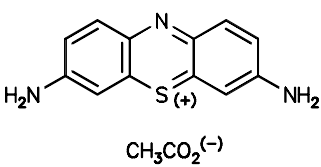
where b is the constant of the Langmuir isotherm ($dm^3\ mg^{-1}$), C_{eq} is equilibrium liquid-phase concentration of the unadsorbed (free) dye (mg dm^{-3}), q_{eq} is equilibrium solid phase concentration of the adsorbed dye and Q is maximum adsorption capacity of the sorbent (both in mg cm^{-3} for calculations based on the settled volume of the magnetic



Rubin S



Safranine O



Thionin

FIG.2
(*Continued*)

sorbent, or in mg g^{-1} for calculations based on dry weight of the sorbent), k is the constant of the Freundlich isotherm.

Equilibrium sorption isotherms were evaluated according to a system of classification of the solution adsorption isotherms described by Giles et al.[11]. From the Fig. 4 it can be seen that isotherms for aniline blue, Bismarck brown Y, congo red, crystal violet and methylene blue follow the typical Langmuir adsorption pattern and belong to the class L2. It was confirmed by the linear transformation of the data used for the construction of adsorption isotherms (see Fig. 5). On the other hand, isotherm for thionin belongs into L3 class and those for rubin S and safranine O into C class. These three dyes (and for low equilibrium concentrations also congo red and crystal violet, the sorption of which was described by the Langmuir model) followed the typical Freundlich model (see Fig. 6).

Both adsorption models are based on different assumptions. It is supposed in the Langmuir model that sorbate is chemically adsorbed at a fixed number of well defined sites, all of them being energetically equivalent. Each active site can hold one sorbate molecule. The sorbate molecules already bound on the surface of the sorbent do not interact themselves nor with the sorbate molecules present in the solution. Monomolecular layer of sorbate molecules is formed on the sorbate surface. On the contrary,

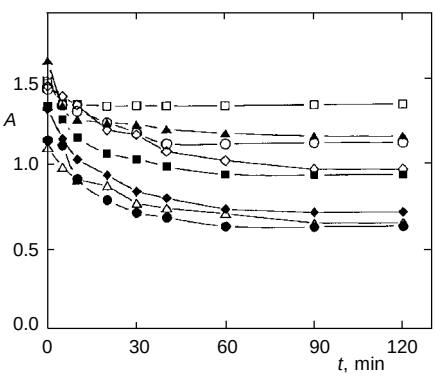


FIG. 3
Time dependence of the adsorption of the tested dyes on magnetic PODMP. For symbols, see Fig. 4. t Time of adsorption, A absorbance of supernatants

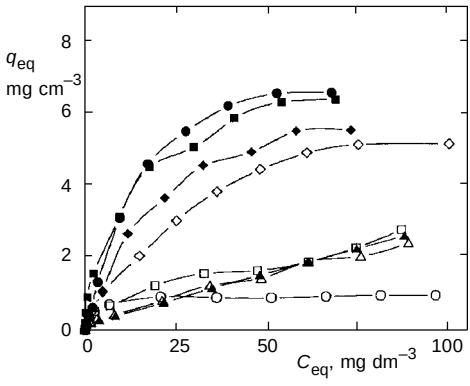


FIG. 4
Equilibrium sorption isotherms of aniline blue (●), Bismarck brown Y (◆), congo red (✧), crystal violet (■), methylene blue (○), rubin S (▲), safranine O (Δ) and thionin (❒) using magnetic PODMP as sorbent. C_{eq} Equilibrium liquid-phase concentration of the unadsorbed (free) dye (mg dm^{-3}), q_{eq} equilibrium solid-phase concentration of the adsorbed dye (dye uptake) (mg cm^{-3})

TABLE I

Maximum adsorption capacities (Q) and Langmuir constants (b) calculated from the Langmuir equation. Magnetic PODMP was used as a sorbent. Q' and Q'' are maximum adsorption capacities calculated for pure dyes. The values in upper lines (without parentheses) are calculated using the settled volume of the magnetic sorbent; the values in parentheses are calculated using the dry weight of the sorbent

Dye	Q mg ml^{-1} (mg g^{-1})	Q' mg ml^{-1} (mg g^{-1})	Q'' μmol ml^{-1} (μmol g^{-1})	b l mg^{-1} (l mg^{-1})
Aniline blue	8.55 (40.32)	6.41 (30.24)	8.69 (40.99)	0.057 (0.057)
Bismarck brown Y	7.52 (35.47)	4.21 (19.86)	10.04 (47.37)	0.041 (0.041)
Congo red	6.49 (30.63)	3.25 (15.32)	4.66 (21.99)	0.040 (0.040)
Crystal violet	6.69 (31.57)	5.02 (23.68)	12.30 (58.04)	0.169 (0.169)
Methylene blue	0.87 (4.13)	0.66 (3.09)	2.01 (9.67)	0.597 (0.597)

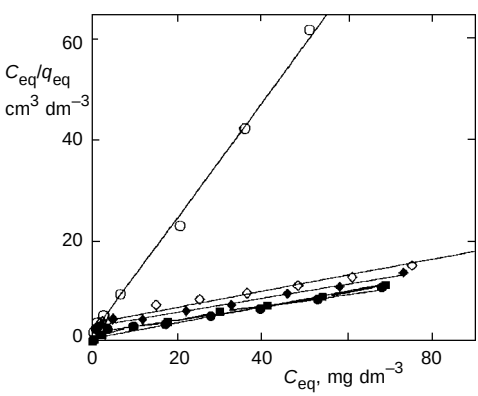


FIG. 5

Langmuir transformation of equilibrium sorption isotherms for aniline blue, Bismarck brown Y, congo red, crystal violet and methylene blue (magnetic PODMP used as sorbent). The symbols and legends are the same as in Fig. 4

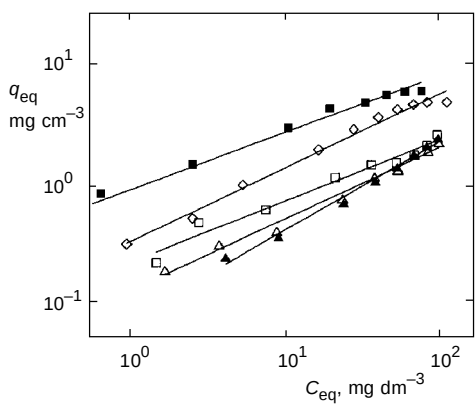


FIG. 6

Freundlich transformation of equilibrium sorption isotherms for congo red, crystal violet, rubin S, safranine O and thionin (magnetic PODMP used as sorbent). The symbols and legends are the same as in Fig. 4

Freundlich model is an empirical one, formulated on the basis of the measured adsorption data.

Maximum adsorption capacities (Q) have been calculated for dyes behaving according to the Langmuir model; the results are shown in Table I. The highest adsorption exhibited triphenylmethane dyes aniline blue and crystal violet, followed by azo dyes Bismarck brown Y and congo red. Methylene blue, belonging to the group of heteropolycyclic dyes, adsorbed only to a small extent. Due to fact that the used dyes were not pure substances, corrected maximum adsorption capacities Q' (mg cm^{-3} or mg g^{-1}) and Q'' (μmol cm^{-3} or μmol g^{-1}) were calculated using the purity of dyes stated in experimental section.

Elution of adsorbed dyes from magnetic PODMP has been tested with water, methanol, 2-propanol, acetone and acetonitrile. The elution of the adsorbed dyes was performed without preliminary removal of weakly-bound dyes. It can be seen from Table II that water desorbes substantial amount of adsorbed dyes. From the organic solvents tested, methanol seems to have the best elution efficiency.

DISCUSSION

As can be seen from the results, PODMP can be simply converted into its magnetic derivative. In the magnetic form this linear polymer can be simply removed from the solutions and suspensions using an appropriate magnetic separator.

There are considerable differences in the sorption of the individual dyes tested. Heteropolycyclic dyes tested (methylene blue, safranine O and thionin) exhibited rela-

TABLE II
Elution efficiency of eluting solvents

Dye	Elution efficiency, %				
	H_2O	CH_3OH	$(CH_3)_2CHOH$	$(CH_3)_2CO$	CH_3CN
Bismarck brown Y	15.3	94.9	70.4	64.2	60.3
Congo red	34.2	55.3	39.1	43.4	42.5
Crystal violet	24.1	42.1	35.9	33.4	34.8
Methylene blue	25.6	31.3	36.5	26.0	32.2
Rubin S	58.7	66.4	41.2	52.1	42.5
Safranine O	31.1	39.6	46.2	50.6	43.4
Thionin	27.6	85.8	36.0	54.7	38.5

tively low adsorption. On the other hand, majority of the triphenylmethane dyes tested (crystal violet and aniline blue) and both azodyes (congo red and Bismarck brown Y) exhibited better sorption to the magnetic PODMP. However, it is rather difficult now to speculate about the relations between the chemical structure of the sorbate molecules and their adsorption on magnetic PODMP. The presence of impurities in the commercial preparations of dyes can also influence their sorption on magnetic PODMP. Other groups of organic compounds will be tested in the near future.

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