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POLYETHYLENE POWDER AS AN ADSORBENT FOR COMPLEXING DYES: INFLUENCE OF DYE STRUCTURE, SOLVENT, pH, AND IONIC STRENGTH

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ABSTRACT

The application of polyethylene (PE) powder to the adsorption of complexing dyes has been studied. Rhodamine B, aluminon, *o*-phenanthroline and dithizone were used as model substances of cationic, anionic, slightly polar, and apolar species, respectively. The influence of PE type, solvent, pH, and ionic strength on the adsorption was investigated. The results showed that high-density PE adsorbs polar dyes, preferentially cationic dyes, from aqueous solutions, whereas low-density PE adsorbs apolar dyes from an apolar milieu. The adsorption of polar species occurs probably at negatively charged sites on the PE surface, whereas the apolar ones occurs at the apolar parts of the surface. Presence of salts and pH influence the adsorption, mainly of anionic dyes; for these, the lower the pH the higher the adsorption, showing that the undissociated anionic dye is adsorbed. The adsorption in ethanolic solutions was very weak, probably because ethanol, differently

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from water, wets PE and therefore competes with the dyes for the active sites on the PE surface. Complexes formed by metallic ions and dyes are also adsorbed on PE showing that, for analytical purposes, metallic cations can be separated from their matrix solutions using adequate PE and conditions for the separation.

Key Words: Adsorption; Dyes; Polyethylene powder

INTRODUCTION

Adsorbents find use in many procedures. Active charcoal is used either for gas absorption, as a clarifying agent, or for analytical purposes of metal concentration and separation. The same occurs with silica, in which adsorbent properties have been used as a desiccant agent, as a support, and a stationary phase for thin layer, gas, and liquid chromatography, and also as sorbent for solid extractions.

Separations through sorption procedures can be conducted considering only the species that will be retained by the adsorbent or considering the effluent obtained after the separation of the species adsorbed. The first procedure includes the use of adsorbents for analytical purposes of species separation or trace concentration, and the second one for the cleaning of wastes, for example by adsorbing dangerous species from any specific milieu.

Polyethylene (PE) could be satisfactorily used as an adsorbent but this property has not been explored very well. Only a small number of works dealt with the use of PE as an adsorbent. It has already been used as a solid support and a stationary phase in liquid chromatography for separation of fatty acids (1), plant extracts (2), and long-chain alcohols (3).

Among the commonly solid sorbents, PE powder possesses the characteristics of an ideal sorbent. It is chemically stable even in the presence of alkalis or acids, and does not dissolve in the most organic solvents. It can be obtained in a high purity degree or easily purified, and it is a very cheap material.

In a previous work, with complexing agents for aluminum, we observed that some dyes were strongly adsorbed on the surface of PE laboratory materials. Considering this property, PE powder could be applied to the separation of trace quantities of analytes from samples as concentrates for hemodialysis (5), blood (4), and salts of p.a. purity degree (6).

On the other hand, dyes can be seen—besides a vehicle for metal separation through complex formation—as species to be separated themselves. For example, the removal of color of waste water from textile industry is an environmental and economic problem (7). It is estimated that about 15% of the world production of dyes is lost into the environment in any step of synthesis, processing, and use of these products (8). Technologies for the treatment of effluents have been receiving increased attention due to the strengthening of environmental laws (8). Techniques for discoloring waste water from dying industry include processes of adsorption, precipitation, chemical degradation, photochemistry, biodegradation and others (9,10). The use of adsorbents includes active charcoal, silica-gel, bauxite, and ion-exchange resins. Some of these are expensive materials as ion-exchange resins, or of difficult regeneration and reuse because the desorption procedure often destroys the adsorbent active surface or deactivate the surface by irreversible adsorption.

The aim of this work is to carry out a systematic study of the adsorbent properties of PE using four dyes or complexing agents as model substances. The adsorption of rhodamine B (RB) (cationic dye), aluminon (AM) (anionic dye), *o*-phenanthroline (PHEN) (slightly polar), and dithizone (DZ) (apolar) on PE was investigated regarding PE density and surface condition, solvent, pH, ionic strength, and, the presence of metals.

EXPERIMENTAL

Materials

A Lambda 16 UV/Vis spectrophotometer (Perkin Elmer, Überlingen, Germany), a SpectrAA-200 atomic absorption spectrometer (Varian, Melbourne, Australia), a Digital DM 20 pH meter (Digimed, São Paulo, Brasil), and a MS-Reglo peristaltic pump (Ismatec, Zurich, Switzerland) were used.

High-density polyethylene (HDPE) and low-density polyethylene (LDPE) were obtained from PPH Company (Pólo Petroquímico de Triunfo—RS, Brazil) already as powder. They were sieved and the 60-mesh portion was used in the experiments.

The complexing agents. RB, AM, PHEN, and DZ were of analytical grade (Merck, Darmstadt, Germany) as well as the solvents, absolute ethanol, methanol, carbon tetrachloride, and tetrachlorethylene. The water used was purified in a Milli-Q system (18.2 MΩ cm) (Millipore, Bedford, USA).

Buffer solutions pH 2.2, 4.0, and 6.0 were prepared with mixtures of citric acid (0.1 mol/L) and sodium hydrogenophosphate (0.2 mol/L) in the following ratios: 19.60:0.40, 12.29:7.71, and 7.37:12.63, respectively.

Solutions of KCl and $CaCl_2$ were used for keeping the ionic strength at 0.5 and 1.5 mol/L, respectively.

Solution of metallic cations were obtained from $TlNO_3$, $Be(NO_3)_2$, $(Co(NO_3)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$, all from Merck. The solutions were prepared in a concentration of 1.0×10^{-2} mol/L.

Procedures

The experiments were carried out with high density polyethylene treated (HDPE) and low density polyethylene treated (LDPE), and with both types after being subjected to an oxidative process with nitric acid. For the oxidation of PE surface, 15 g of each PE was mixed with 100 mL 15% (v/v) aqueous HNO_3 and left to shake for 24 hr. After that the PE was washed and dried at 70°C for 2 h.

All experiments were carried out measuring the absorbance of the solutions of the dyes before and after being in contact with PE. The dye concentration was calculated using analytical curves. The difference between the concentrations was converted into mass or number of moles. As PHEN itself does not absorb in the visible region, the measurement of its concentration was carried out after adding Fe(II) ions into the solution. A 1.0×10^{-2} mol/L solution of $FeSO_4{\cdot}7H_2O$ was used, and 500 μL of this solution was added to 5 mL of PHEN solution in both cases, before and after the contact with PE.

The solvents used for adsorption tests were water and absolute ethanol for RB, AM, and PHEN, and absolute ethanol and carbon tetrachloride for dithizone.

The adsorption experiments were done with solutions containing 250 μmol/L AM and PHEN and 30 μmol/L RB and dithizone, separately. These concentrations were chosen in order to have measurable absorbance values without further dilution. In all experiments the temperature was kept at 25°C.

Adsorption Equilibrium Rate and Isotherms

Six milliliters of solution of AM and PHEN (250 μmol/L) and of RB and DZ (30 μmol/L) was placed separately with 1.0 g PE in a screw cap glass tubes. After time intervals of 15, 30, 60, and 90 min, the suspension was filtered through a Gooch-type crucible n° 3 (glass fritted disc, 40 mm diameter) and the absorbance of the solution measured at its maximum, 530 nm for AM, 560 nm for RB, 510 nm for PHEN (in presence of Fe II ions), and 605 nm for DZ.

Isotherms were obtained from aqueous solutions at ionic strength, 0.5 mol/L (KCl) with HDPE for RB, AM, and PHEN. The isotherm for DZ was obtained in ethanolic solution with LDPE.

Influence of PE Type and Surface Treatment, pH and Ionic Strength

For the experiments, 6.0 mL of the solution was placed in a screw cap glass tube (15 mL capacity) with 1.0 g PE and left to shake for 30 min. After this period, the solution was filtered and its absorbance measured.

The influence of the PE type on the adsorption was tested in water and in ethanol for RB, AM, and PHEN and in ethanol and in CCl_4 for DZ.

The adsorption of RB, AM, and PHEN was tested for three pH values: 2.2, 4.0, and 6.0 and at two different ionic strengths, 0.5 and 1.5 mol/L, fixed with KCl, with all PE types.

The adsorption of RB, AM, and PHEN was also carried out in the presence of mono- (K^+) and divalent (Ca^{2+}) cations at the same molar concentration (0.5 mol/L).

Elemental Analysis

All PE used in this experiment, HDPE, LDPE, and those subjected to the oxidative treatment, were analyzed for their carbon, hydrogen, and oxygen content. The analysis was carried out in an Analysensysteme GBmH (Hanau, Germany) elemental analyzer.

Infrared Spectra

For this analysis, 0.125 g PE was dissolved in 25 mL of tetrachlorethylene by heating it to the boiling temperature for 8 hr (11). The infra-red (IR) spectrum was obtained with a film done with an aliquot of this solution. The spectra were collected in an Bruker IFS 28 (Bremen, Germany) infrared spectrometer.

Adsorption of Metallic Complexes

The investigation was carried out in presence of an excess of metallic cation in relation to the dye. Beryllium was complexed by AM, thallium by RB, iron by PHEN, and cobalt by DZ. Six milliliters of solution of each dye containing 1.0 mmol/L of its respective metal was placed with 1.0 g PE in a glass tube and the adsorption experiment with all PE was carried out as described above.

Column Experiments

Columns were packed using glass tubes (0.8 × 10 cm) with about 5 g PE. Flow rates from 0.5 to 2.0 mL/min were selected by means of a peristaltic pump. The experiments were carried out with aqueous and saline solutions (0.5 mol/L KCl) of pure dyes and in the presence of trace quantities (50 μg/L) of metallic cations. Sample volume of 100 mL was assayed. The following solutions were used for 100 mL aqueous sample: AM, 15 mL solution 0.05% (m/v); RB, 0.1 mL solution 0.5% (m/v); PHEN, 1.0 mL solution 0.25% (m/v); DZ, 5.0 mL sol 25 μmol/L in 100 mL CCl_4. Conditions for metal complexation were the standard conditions recommended by Snell (12).

In order to quantify the retention of metallic cations, after the sample adsorption, the column was washed with 10 mL water and the elution carried out with 10 mL of an acidified solution of ethanol (0.3% HNO_3 in absolute ethanol, v/v) for AM, PHEN, and DZ. The RB was eluted with 10 mL of methanol. Metals in eluate were measured by flame atomic absorption spectrometry (FAAS, Überlingen, Germany), following the standard parameters (wavelength, gas) for these elements programmed in the instrument.

The experiment with DZ was carried out extracting 50 μg/L cobalt from 100 mL aqueous saline solution into 100 mL DZ/CCl_4 solution and passing 50 mL of the organic phase through the column. The elution was carried out as described above.

All the described experiments were carried out in triplicate and the results are mean values of these measurements.

RESULTS AND DISCUSSION

The results showed that after 15 min, the adsorption equilibrium was attained and therefore a time of 30 min was chosen for the experiments. The adsorption isotherms in Fig. 1 show that the concentration of the dyes chosen for the experiments are in a range where little changes in the concentration do not produce changes on the adsorbed amount of the dye.

Influence of the Solvent

Water and ethanol were used as solvent for RB, AM, and PHEN, and ethanol and CCl_4 for DZ. The results shown in Table 1 are those obtained with HDPE. The results from the other PEs were not shown; the difference in the relative adsorbed amount of each dye, between the different PEs, was the same. The results in Table 1 show that whereas 89% of RB and 30% PHEN are adsorbed from aqueous solutions, none of the AM was adsorbed. Only 10% of RB and 6% of PHEN were adsorbed from ethanolic solutions, and practically the same 10% of AM. The DZ was more adsorbed from CCl_4 solution (63%), than from ethanolic solution (26%). It can be concluded that polar dyes show more affinity for PE when in aqueous solution. Either they have more affinity for the less polar PE surface than for the more polar aqueous milieu, or this could also be

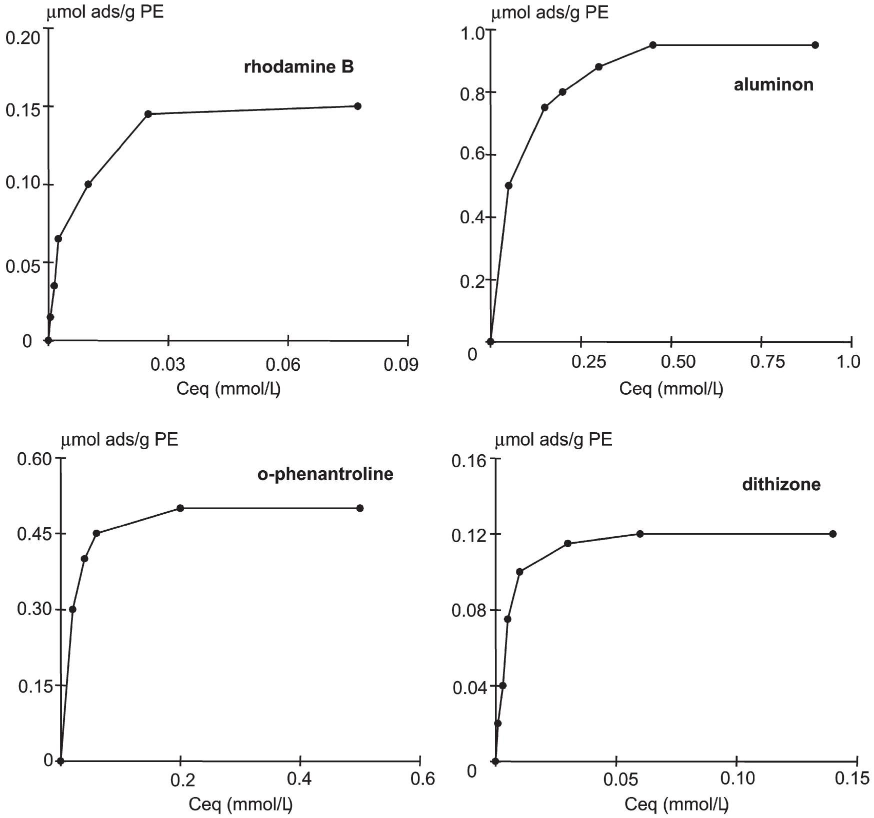

Figure 1. Adsorption isotherms of AM, RB, and PHEN on HDPE in aqueous solutions. Ionic strength 0.5 mol/L. Adsorption isotherm of DZ on LDPE in CCl_4 solution.

a result of the wetting of the PE surface by the solvents. As water does not wet PE, the adsorption of the dyes is favored; on the other hand, ethanol wets PE and therefore it competes with the dyes for the active sites of the adsorbent. This effect also occurred with CCl_4.

Polyethylene

The oxidation of PE is associated with the generation of oxygen-containing species on the chain at branch points (13,14). Hydroxyl, carbonyl, carboxy, peroxo, hydroperoxo, and other groups have been detected at PE surface. Studies with PE samples subjected to oxidation showed that the polar dye methylene blue

Table 1. Adsorption of Dyes on High-Density Polyethylene from Aqueous and Ethanolic Solutions

	% Adsorbed	
Dye	Aqueous Solution	Ethanolic Solution
Rhodamine B	89 ± 3	10 ± 2
Aluminon	0.2 ± 0.5	12 ± 3
o-Phenantroline	30 ± 1	6 ± 3
Dithizone	63 ± 2[a]	26 ± 3

Initial concentration of the dye: 30 μmol/L RB and DZ, and 250 μmol/L AM and PHEN. Results expressed as percentage adsorbed dye per gram PE.

[a] In CCl_4.

stained the oxidized parts whereas Sudan III, an apolar dye, stained the nonoxidized ones (15). Consequently, because of its apolar nature, PE adsorbs apolar substances; however, when PE is subjected to any process that leads to the formation of oxidized sites, polar substances are able to be adsorbed on these sites.

The HDPE and LDPE utilized in this work were subjected to an oxidative treatment with nitric acid, and the experiments carried out with the four PE: high- and low-density, with and without oxidative treatment. In order to characterize the changes on the PE surface after the oxidative treatment, elemental analysis and IR spectra of the four PE were done. The purpose was to observe the possible introduction of oxygen-containing groups onto the surface. However, the elemental analysis and the IR spectra had not shown significant difference before and after the treatment. The difference on the oxygen percentage showed by the elemental analysis were within the experimental error of the technique, and the IR spectra also did not show clear features that could be attributed to groups arising from the oxidation of the PE. Probably the formation of new oxidized sites on the PE surface was enough to change the adsorption of the dyes but not to change the ratio C:H:O. Considering that the oxidation occurred only at the surface of a PE particle and that whole of it was dissolved for the IR measurement or consumed in the elemental analysis, the oxygen introduced by the oxidation is really a very small percentage of the total mass.

The formation of oxidized sites was not confirmed by IR or elemental analysis; however, the treatment with HNO_3 changed the interaction between dye and PE. The adsorption of polar dyes from aqueous solutions, for either HDPE or LDPE, increased after the oxidative treatment (Table 2), whereas the adsorption of DZ (in CCl_4) decreased after the oxidative process. These results show that the

Table 2. Adsorption of Dyes on HDPE, LDPE, and Both After Oxidative Treatment (LDPET, HDPET), from Aqueous and Ethanolic Solutions

Dye % adsorbed from aqueous solution	LDPE	LDPET	HDPE	HDPET
Rhodamine B	52 ± 5	63 ± 4	89 ± 3	89 ± 1
Aluminon	0.1 ± 0.1	0	0.2 ± 0.5	0.2 ± 0.5
o-phenantroline	8 ± 4	21 ± 2	30 ± 1	43 ± 4
Dithizone[a]	64 ± 2	38 ± 3	63 ± 2	63 ± 1
% adsorbed from ethanolic solution				
Rhodamine B	10 ± 2	0	10 ± 2	2 ± 1
Aluminon	7 ± 5	31 ± 3	12 ± 3	76 ± 3
o-phenantroline	0	16 ± 4	6 ± 3	19 ± 3
Dithizone	53 ± 3	26 ± 2	26 ± 3	16 ± 1

Initial concentration of the dye: 30 μmol/L RB and DZ, and 250 μmol/L AM and PHEN. Results expressed as percentage adsorbed dye per gram PE.
[a] In CCl_4.

surface turns more polar by the oxidation and therefore increases the affinity for polar dyes and decreases the affinity for apolar ones. It can also be concluded that the surface of PE particles was already partially oxidized because polar dyes have been adsorbed on both PE, even before they are subjected to the oxidative treatment.

Influence of pH and Ionic Strength

These experiments were carried out in aqueous solutions of RB, PHEN, and AM. They included solutions of three different pH at two ionic strengths (0.5 and 1.5 mol/L, KCl solution). Experiments were also done in presence of monovalent (K^+) and divalent (Ca^{2+}) cations at the same concentration of 0.5 mol/L. In a previous work, it was observed that the charge of the cation, more than its concentration, could affect the adsorption. Chrome azurol S was more tightly adsorbed from solutions of $CaCl_2$ and $MgCl_2$ than from solutions of KCl, NaCl, and NaAc (3).

Neither pH nor the ionic strength produced changes in the behavior of RB (Fig. 2), probably due to its ionic structure, it was less affected by the presence of other ions in solution or changes in pH. The adsorption of PHEN is slightly affected by the pH of the solution and by the presence of ions in solution. It seems that in presence of ions the adsorption tends to be diminished. The AM, however, changed its behavior in presence of salts. It was not adsorbed from pure water, but

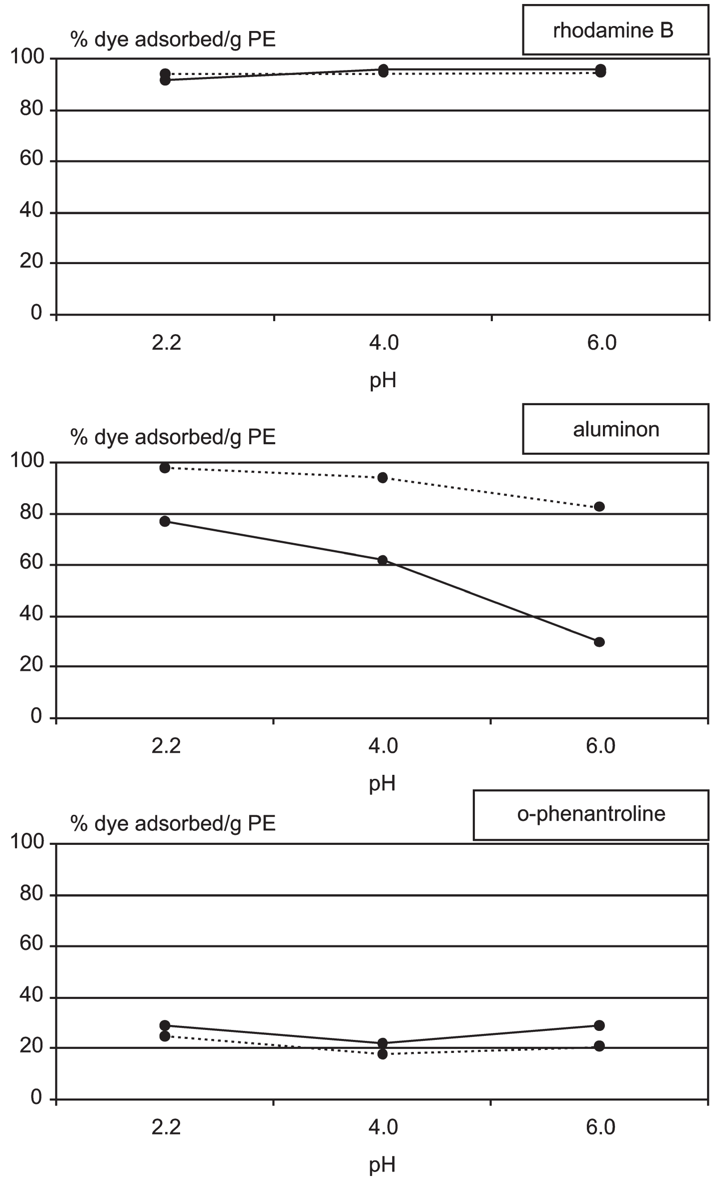

Figure 2. Percentage of dye adsorbed on HDPE at different pH and ionic strength. Ionic strength fixed at 0.5 mol/L (bold line) and 1.5 mol/L (dotted line) with KCl.

it was strongly adsorbed from saline solutions. In addition, pH had an influence on the AM adsorption, the lower the pH the higher the adsorption (Fig. 2). As AM is a salt derived from a weak acid, its dissociation is pH dependent. Low pH represses the dissociation and leads to a decrease in the repulsion between the dye and the active sites of PE surface. On the other hand, the presence of a salt in solution causes a salting out effect that also contributes to increase the adsorption of the dye onto the PE surface. This is similar to the one that occurs in textile industry, where large amounts of NaCl or Na_2SO_4 are used for the fixation of anionic dyes on cellulose fibers (7,16,17). There was a difference in the adsorption in presence of mono- or divalent cations, but it seems related more to the ionic strength of the solution than to the charge of the cation.

Comparing the amount of each dye adsorbed in solution of KCl and $CaCl_2$ at the same molar concentration (0.5 mol/L) (Fig. 3), it can be seen that it is higher in $CaCl_2$ solution only for AM. However, considering the ionic strength of the solutions, when they are the same for both cation solutions (1.5 mol/L), the extent of the adsorption is practically the same (compare Figs. 2 and 3).

All experiments were carried out with all four PE types and the results for each dye were alike. For simplicity, only the set of one PE type has been showed. As already mentioned, from one PE to another changes the amount adsorbed but not the behavior; for example, AM was adsorbed by all PE when in presence of salts, and only small differences were observed among these results. The percentage of the dye adsorbed from solutions of KCl, when the pH changed from 2.2 to 6.0, decreased from 77.4 to 29.5% for HDPE and from 83.3 to 21.4% for LDPE.

Adsorption of Metallic Complexes

For analytical purposes of metal pre-concentration and separation, the dye must complex the metallic cation quantitatively and in this way be adsorbed on PE. On the other hand, considering only the dye separation, the presence of metallic cations should not interfere with the dye adsorption.

The experiments were carried out using metallic cations in excess to the dye. The pH of the solutions was kept at the value appropriate for the complexation. For DZ, an aqueous solution of cobalt was put in contact with the CCl_4–DZ solution and, after shaking, the CCl_4 phase was subjected to the assay with PE. Table 3 shows the results of the adsorption in presence and absence of metals. These experiments were also carried out with all PE, but only the result of one type is showed. The change produced by the complex formation occurred in the same way for each PE, increasing or decreasing the amount adsorbed at the same rate. Indeed, there was no significant difference on the adsorption of the dye or its complex, except for AM. In this case, changes in ionic strength and pH of

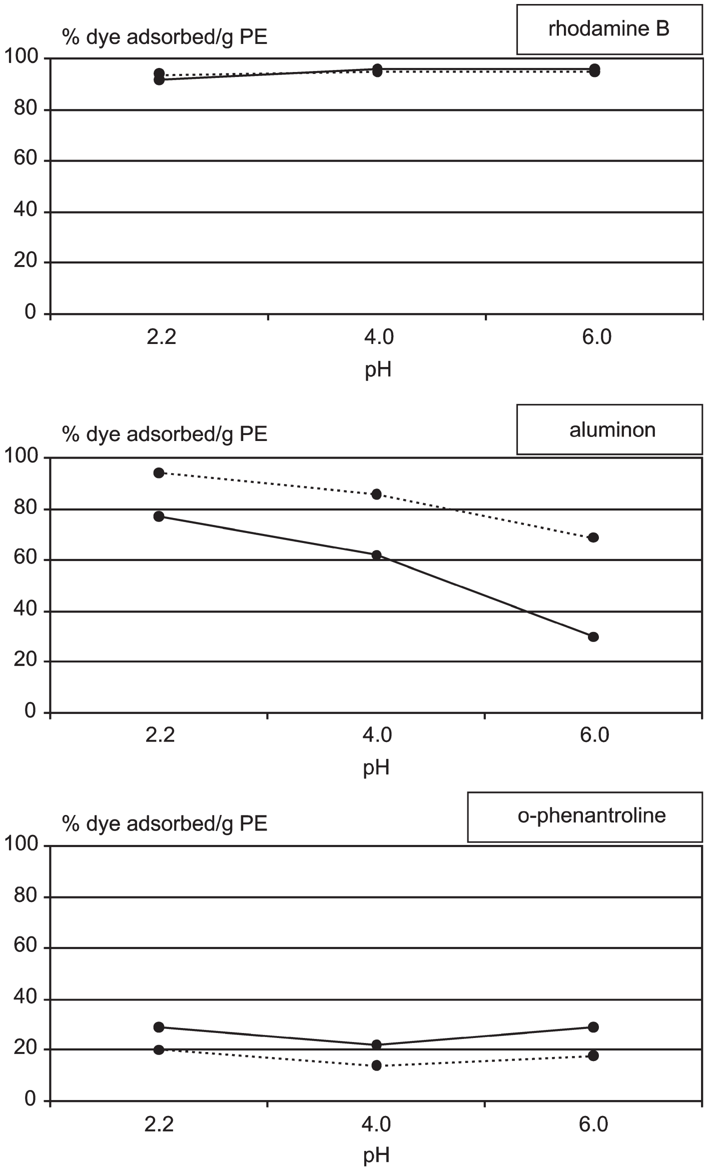

Figure 3. Percentage of dye adsorbed on HDPE at different pH and in presence of a monovalent (K) and a divalent (Ca) cation at the same concentration of 0.5 mol/L. Bold line KCl solution, dotted line $CaCl_2$ solution.

Table 3. Adsorption of RB, AM, and PHEN on HDPE from Aqueous Solution and DZ on LDPE from CCl_4 Solution in Presence of an Excess of a Metallic Cation

		% Adsorbed	
Dye	Metal	Without Metallic Cation	With Metallic Cation
Rhodamine B	Tl	89 ± 3	91 ± 7
Aluminon	Be	0.2 ± 0.5	67 ± 4
o-Phenantroline	Fe	30 ± 1	21 ± 2
Dithizone	Co	63 ± 2	60 ± 2

Results expressed as percentage adsorbed dye per gram PE.

the solution, due to the presence of ions from salts (metal and buffer) and complex formation, turned, as above, the dye able to be adsorbed.

Column Experiments and Metal Pre-concentration

The HDPE was used for RB, PHEN, and AM and LDPE for DZ. Considering the adsorption capacity of each PE, solutions were prepared to have the adequate excess of the dye in relation to the metal, but not to exceed the column capacity.

Five grams of PE was enough for the retention of all dyes (100 mL solution), however, due to the different behavior of the dyes in pure water and saline solutions, higher flow rates could be used for saline solutions. This is not related to DZ, which was adsorbed from a CCl_4 solution. Table 4 is a summary of the experimental conditions and results for column runs.

Flow rates up to 2 mL/min can be used either for pure aqueous solution or for saline solution. From saline solutions, stronger interaction dye/column was observed, not only for AM, but also for PHEN and RB. Whereas from pure aqueous solution, the dyes spread onto practically all PE in the column, from saline solution they were retained just in the first part of the column. The columns became almost totally (aqueous solution) or partially (saline solution) colored by the dye. In this way, flow rates up to 5 mL/min could be used for saline solutions of AM and RB and up to 2 mL/min for PHEN. For DZ, flow rates up to 2 mL/min allowed the retention of all dye. The adsorption in column differed a little from that in batch. A salting out effect, that in batch experiments was observed only for AM, was also observed for PHEN and RB; and for AM, this effect was stronger in column than in batch.

Table 4. Adsorption of Pure Dyes and Metallic Complexes in PE Columns (0.8 × 10 cm, 5 g) from Aqueous and Saline Solutions

	AM			RB			PHEN			DZ
	Aqueous	KCl	KCl–Be	Aqueous	KCl	KCl–Tl	Aqueous	KCl	KCl–Fe	Co
Flow rate for total retention (mL/min)	n.a.	5	5	2	5	5	1	2	2	2
Metal recovery (%) ($n = 3$)	—	—	98 ± 4	—	—	98 ± 2	—	—	102 ± 2	101 ± 3

n.a. = No adsorption.

Saline solution: KCl 0.5 mol/L. Metal concentration: 50 μg/L. Volume solution: 100 mL. Eluent (10 mL): methanol for RB and 0.3% HNO_3 in absolute ethanol (v/v) for AM, PHEN, and DZ.

The results of metal pre-concentration (Table 4) showed that if the dye was quantitatively retained (effluent colorless), the metal was quantitatively retained too. All metals were recovered and an enrichment factor of 10 was achieved.

CONCLUSION

The PE powder, a stable and cheap material, can satisfactorily be used for separation of dyes and their metallic complexes due to the adsorption of both dye and complex on the PE surface.

This adsorption can be related to the structure of PE and to the presence of oxidized sites on the PE surface, associated with the structure of the dyes. The HDPE, that has a structure more crystalline than LDPE, adsorbs preferably polar dyes, whereas LDPE, the apolar ones.

As RB (cationic dye) and DZ (apolar) were adsorbed on HDPE and LDPE, respectively, it can be concluded that HDPE has more polar sites than LDPE and that the adsorption occurs on negatively charged sites on the surface of HDPE. The adsorption of AM supports this point because it is an anionic dye and its adsorption occurs at low pH and in presence of salts, where its dissociation is repressed.

Metals does not avoid the adsorption, complexes can be adsorbed as good as the complexing agents, showing that the retention occurs even when the dye is bonded to a metallic cation. The adsorption of complexes also shows that PE can be used for separation and pre-concentration of metals. Separations can be carried out even from saline solutions because of the presence of salts not only does not interfere on the adsorption of the complex but also enhances it. The weak adsorption of the dyes in ethanolic solution is, for analytical purposes, worthy because ethanol can be used as an eluent of the adsorbed complexes for their further quantification, or the elution of dyes with ethanol can lead to their recovery after any procedure of dye production or of dying of fibers.

The results of column experiments also confirmed the influence of salts in the adsorption of the dyes, the possibility of metal pre-concentration, and the use of alcoholic solutions as an eluent. Column pre-concentration allowed the determination of metal trace quantities from saline solutions for example by FAAS without interference.

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