Screen-printed zeolite-modified carbon electrodes

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The evaluation of screen-printed carbon electrodes modified with zeolites for the determination of the herbicides paraquat and diquat is described and compared to the corresponding zeolite-modified carbon paste electrodes. Cyclic voltammetry was used to characterise the electrochemical behaviour of paraquat at both electrodes, indicating better defined peaks for the screen-printed electrodes than for the corresponding carbon pastes and lesser influence of residual oxygen. Square wave voltammetry was then applied to investigate the partitioning of this herbicide into the zeolite particles (Y-type) to the conductive composites. The screen-printed zeolite-modified electrode (SPZME) resulted in faster accumulation and release of the electroactive probe compared to the zeolite-modified carbon paste electrode (ZMCPE). The improved response time, sensitivity, and reproducibility, were attributed to the thin film structure of SPZME compared to the bulky ZMCPE. Substantial enhancement of current signal was observed when operating with disposable SPZMEs that were not soaked in any electrolyte solution prior to the accumulation step. The selective accumulation of paraquat over diquat was demonstrated by using ZSM-5 zeolite particles, while its strong binding to the aluminosilicate prevented efficient voltammetric detection.

Introduction

Zeolites are attractive electrode modifiers because their presence at an electrode surface allows the combination of selected electrochemical reactions with intrinsic zeolite properties such as size and shape selectivities, ion exchange capacity, or catalytic activity.[1] Zeolite-modified electrodes (ZMEs) have generated great interest during the past 15 years, finding numerous applications especially in electroanalysis.[2–4]

Because zeolites are crystalline in nature and made of solid particles which are not electronically conductive, their use in connection with electrochemistry is not technically easy. This is probably why numerous preparation methods for ZMEs were proposed and assessed previously.[3,5,6] They can be classified into four main categories,[4] including the dispersion of zeolite particles within a conductive composite matrix, the compression of zeolites onto a conductive substrate, the formation of zeolitic films (embedded in or covered by an inert polymer) on solid electrodes, and the covalent binding of zeolite particles to an electrode surface. Such a diversity illustrates that the ideal preparation procedure has not yet been discovered for getting highly durable ZMEs ensuring fully reproducible measurements.[6] This is especially important with respect to the application of ZMEs for analytical purposes. In particular, zeolite films suffer from poor mechanical stability preventing their use in stirred solution, and zeolite-modified carbon paste electrodes, though being largely exploited in electroanalysis,[7–12] were reported to undergo imbibition of the bulk paste by the surrounding solution,[8,13] hindering somewhat the chemical regeneration of the electrode surface (memory effects).

A possible way to get round this difficulty could be found in applying the screen-printing technology, which was successfully used for constructing disposable electrochemical sensors and biosensors in the last decade.[14–18]

The present study aims to prepare screen-printed zeolite-modified carbon electrodes and apply them to the preconcentration/voltammetric measurements of paraquat and diquat. Zeolite Y was chosen as a representative crystalline aluminosilicate which is known to incorporate these herbicides by ion exchange.[19] The main purpose of this paper is to show how this new type of zeolite-modified electrode can overcome some drawbacks encountered with zeolite-modified carbon paste electrodes applied in the accumulation–voltammetric detection scheme. Special attention will be given to the ability to chemically regenerate the electrode surface after the measurement. A particular zeolite ZSM-5 will be tested as a selective sorbent for paraquat over diquat.

Experimental

Apparatus and reagents

Electrochemical experiments were performed in a three-electrode cell configuration. Working electrodes were laboratory-made screen-printed or carbon paste electrodes modified with zeolite particles. The counter-electrode was made of a platinum wire, and the Ag/AgCl electrode (Metrohm, Herisau, Switzerland) was used as reference. Electrochemical studies were conducted with the EG&G Princeton Applied Research (Princeton, NJ, USA) Model 283 potentiostat/galvanostat monitored by the Model M270 software (EG&G).

All reagents and electrolytes were of analytical grade and all solutions were prepared with high purity water (18 MΩ cm^{-1}) from a Millipore (Watford, Herts., UK) Milli-Q water purification system. Paraquat (methyl viologen dichloride hydrate, N,N'-dimethyl-4,4'-bipyridinium dichloride) was purchased from Aldrich (Bornem, Belgium), and diquat (1,1'-ethylene-

2,2′-bipyridinium dibromide) was an analytical standard Pestanal® (Riedel-de Haën, Hannover, Germany). Zeolite Y was Linde Molecular sieve Cat. Base L-Y54 powder (UOP, Molecular Sieve Division, Des Plaines, IL, USA) used in its sodium form (formula: $Na_{56}Al_{56}Si_{136}O_{384}\cdot 250\ H_2O$). Zeolite ZSM-5 was obtained from the Laboratoire des Matériaux Inorganiques (Namur, Belgium) and its chemical composition was $Na_4Al_4Si_{92}O_{192}\cdot \sim 16\ H_2O$.

Preparation of zeolite-modified electrodes

Screen-printed zeolite-modified electrodes (SPZMEs) were fabricated by using a semi-automatic screen printer (Model TF 100, MPM, Franklin, MA, USA). Samples of zeolite particles were first added to the carbon ink (Ercon ink G-449-I, Ercon, Waltham, MA, USA) in selected ratios and the resulting materials were hand mixed thoroughly (with a spatula) for 30 min, until homogeneous dispersions were obtained (note that the specified zeolite loadings refer to the initial ink composition, prior to the solvent evaporation). These modified inks were printed through a patterned (100 μm thick) stencil onto 10 × 10 cm alumina ceramic plates containing 30 strips (each being sized 3.33 × 1.00 cm, as defined by a laser pre/semi cut). The resulting 0.2 × 3.0 cm printed structures were cured for 60 min at 80 °C. An insulating ink (Ercon R-486(AH)Blue) was then printed on a portion of the plate (and cured for 60 min at 80 °C), to leave 2 × 5 mm sections on both ends for defining the working electrode and the electrical contact.

Zeolite-modified carbon paste electrodes (ZMCPEs) were prepared as previously described.[9,20] Typically, 0.1 g zeolite and 0.6 g carbon graphite (<325 mesh, Johnson Matthey, Royston, Herts., UK) were thoroughly mixed with 0.3 g of the organic binder (Nujol, Aldrich) for ca. 15 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a home-made PTFE cylindrical tube (od 8 mm, id 6 mm) equipped with a screwing stainless steel piston. When necessary, a new surface was obtained by pushing an excess of paste out of the tube (about 200–500 μm thickness) and polishing it on a weighing paper. Unmodified carbon paste was prepared according to the same procedure without adding zeolite to the mixture and was used for comparison purposes.

Procedures

All experiments were performed at room temperature. Each screen-printed electrode was used either in a single experiment without any preconditioning or in multiple experiments after being immersed in the electrolyte solution (typically 0.1 M NaCl) for 30 min before measurement. The surface of the carbon paste electrodes was mechanically polished prior to each series of experiments. Solutions were purged with pure nitrogen for a selected period of time (see below) before measurements.
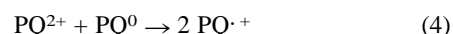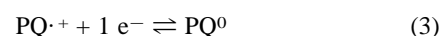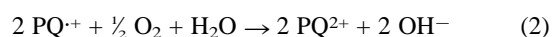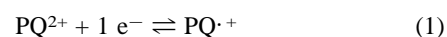
Cyclic voltammetry and square wave voltammetry were applied to evaluate the electrochemical behaviour of the electrodes. Square wave voltammetry was used to monitor the uptake and release of the analytes from the electrodes because of its better sensitivity and detection limit. Due to the rather high value of the uncompensated resistance when using screen-printed electrodes (1–2 kΩ), a correction for ohmic drop was applied by positive feedback. Accumulation was performed at open circuit in the analyte solution, the electrode was then removed and rinsed with pure water, and immersed in the detection cell for recording the voltammetric curve. Regeneration was achieved by soaking the electrode loaded with the analyte in a solution containing 1 M NaCl, at open circuit, until no signal for the analyte was obtained.

Batch ion exchange experiments involving paraquat and diquat in zeolites Y and ZSM-5 were monitored by UV spectrophotometry (spectrophotometer Beckmann DU 7500; Fullerton, CA, USA) in the supernatant obtained after centrifugation of the zeolite suspension. Paraquat was detected at 258 nm and diquat at 309 nm.
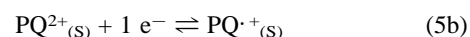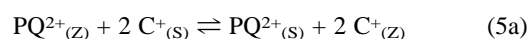
Results and discussion

Electrochemical behaviour of paraquat at unmodified and zeolite-modified carbon electrodes

The electrochemistry of viologen derivatives (such as paraquat, PQ^{2+}; or diquat, DQ^{2+}) has been well-known for a long time on unmodified electrodes,[21] and the electrochemical behaviour of paraquat has been well studied on various types of modified electrodes.[13,22–25] The electro-reduction of PQ^{2+} proceeds *via* the formation of a blue radical cation, $PQ^{\cdot+}$ (eqn. 1), which can reversibly form a dimer.[26] The monoelectronic charge transfer is reversible but the presence of oxygen can induce some complications by reacting with $PQ^{\cdot+}$ species (eqn. 2). The further monoelectronic reduction of $PQ^{\cdot+}$ to the fully reduced state, PQ^0 (eqn. 3), occurs at more negative potentials and is less reversible because of the conproportionation reaction between PQ^0 and PQ^{2+} to generate $2PQ^{\cdot+}$ (eqn. 4), which tends to adsorb on the electrode surface.

$$PQ^{2+} + 1\ e^- \rightleftharpoons PQ^{\cdot+} \qquad (1)$$

$$2\ PQ^{\cdot+} + \tfrac{1}{2}\ O_2 + H_2O \rightarrow 2\ PQ^{2+} + 2\ OH^- \qquad (2)$$

$$PQ^{\cdot+} + 1\ e^- \rightleftharpoons PQ^0 \qquad (3)$$

$$PQ^{2+} + PQ^0 \rightarrow 2\ PQ^{\cdot+} \qquad (4)$$

When incorporated in zeolite Y-modified electrodes, PQ^{2+} is liable to undergo charge transfer reactions,[13,22] which have been demonstrated to proceed after ion exchange for the supporting electrolyte cation, C^+ chosen here as monovalent for convenience, according to an extra zeolite electron transfer mechanism [eqns. 5 (a) and (b)].[27]

$$PQ^{2+}_{(Z)} + 2\ C^+_{(S)} \rightleftharpoons PQ^{2+}_{(S)} + 2\ C^+_{(Z)} \qquad (5a)$$

$$PQ^{2+}_{(S)} + 1\ e^- \rightleftharpoons PQ^{\cdot+}_{(S)} \qquad (5b)$$

where subscripts Z and S refer to zeolite and solution phases, respectively.

Comparison between zeolite-modified screen-printed and carbon paste electrodes

Cyclic voltammetry characterisation. Fig. 1 illustrates typical cyclic voltammograms recorded for PQ^{2+} in solution (after 15 min nitrogen bubbling) by using carbon paste and screen-printed carbon electrodes, respectively unmodified and modified with 10% zeolite Y. Such electrodes will be noted hereafter as CPE (bare carbon paste electrode), ZMCPE (zeolite-modified carbon paste electrode), SPCE (bare screen-printed carbon electrode), and SPZME (screen-printed zeolite-modified electrode). There are several things to notice on this figure, displaying definite advantages of using screen-printed carbon instead of carbon paste. First, the effect of oxygen was less with use of screen-printed electrodes. Second, the presence of zeolites induced a significant enhancement of peak currents. Third, this enhancement was much more intense with SPZME than with ZMCPE.

Purging the solutions with nitrogen during 15 min was sufficient for preventing the effect of oxygen on the electrochemical behaviour of PQ^{2+} when using SPCE or SPZME,

while the electrocatalytic reduction of oxygen by paraquat was clearly visible when using CPE or ZMCPE (cathodic peak located between -0.50 V and -0.55 V) and required several hours for completing the purge. This electrocatalytic wave was otherwise exploited for sensing oxygen at carbon composite electrodes modified with zeolites in the presence of paraquat.[28] After complete deaeration, the two successive reduction steps of PQ^{2+} were chemically reversible (with cathodic-to-anodic peak currents ratio close to unity) but only the first one was electrochemically reversible, as shown in Table 1. The difference in the cathodic and anodic peak potentials was about 60 mV, as expected for a reversible process, indicating fast electron transfer with both electrodes. When using bare electrodes and scanning potentials up to only -0.85 V (limited to the first electron transfer), a plot of the peak currents *versus* the square root of the scan rate produced a straight line ($r^2 = 0.998$) for both cathodic and anodic processes, indicating diffusion-controlled charge transfer reactions.

While the response of bare electrodes was quite independent of the time afforded to the electrode to contact the solution, prolonged soaking of the zeolite-modified electrodes in the PQ^{2+} solution resulted in a marked increase in the peak currents. This is fully explained by the accumulation of PQ^{2+} species at the electrode surface, by ion exchange within zeolite particles. The enhancement was especially outstanding for the second cathodic peak, corresponding to the reduction of $PQ^{\cdot+}$ species (eqn. 3), which was much more intense than the first one (eqn. 1), as compared to the bare electrodes for which the two cathodic peaks are roughly equivalent, giving very different cathodic-to-anodic current ratios (Table 1). This particular voltammetric pattern can be explained by the high reservoir of PQ^{2+} species (in the bulk zeolites), concomitant to the electrochemical generation of PQ^0, inducing the production of

large amounts of $PQ^{\cdot+}$ species (eqn. 4) which are reduced at the electrode surface at about -1.0 V (Fig. 1, curves B and D). Similar behaviour was recently observed by Brunetti and Ugo[25] at glassy carbon electrodes covered by a poly(estersulfonate) ion exchanger.

Interestingly, the enhancement in peak currents observed when passing from bare electrodes to zeolite-modified electrodes was significantly greater with screen-printed electrodes than with carbon paste (look at the scale change on Fig. 1 when passing from SPCE to SPZME). This behaviour was also observed by performing voltammetry in an analyte-free medium after preconcentration at open circuit from a diluted PQ^{2+} solution. For example, Fig. 2 illustrates the case of 1×10^{-6} M PQ^{2+}, analysed by square wave voltammetry after a 30 min preconcentration, indicating a 7.5 enhancement factor for SPZME, compared to 1.7 for the ZMCPE. Such enhancement can be attributed to a higher zeolite loading (in view of the solvent evaporation during the curing step).

Trace analysis by square wave voltammetry

Release and uptake of paraquat in zeolite Y. ZMCPEs have been applied in the past for electroanalytical determinations based on the preconcentration–voltammetric detection scheme,[7,9,29,30] but their chemical regeneration (by back ion exchange) is known to be rather difficult due to the progressive imbibition of the paste interior by the surrounding solution.[12,13] This is illustrated in Fig. 3 (curve a) where more than 70% of the initial signal of preconcentrated paraquat was maintained even after prolonged soaking of the electrode in the electrolyte solution. By contrast, the use of SPZMEs resulted in much
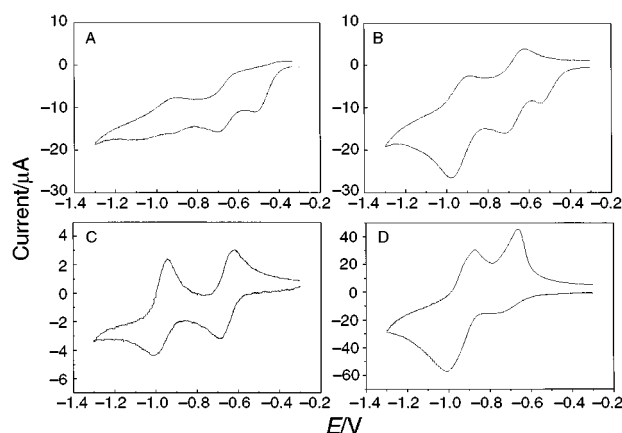

Fig. 1 Cyclic voltammograms for 2.0×10^{-4} M paraquat at bare carbon paste electrode (A), 10% zeolite Y-modified carbon paste electrode (B), bare screen-printed carbon electrode (C), and 10% zeolite Y-modified screen-printed carbon electrode (D), after 15 immersions of the electrodes into the solution (under bubbling with pure nitrogen). Supporting electrolyte: 0.1 M NaCl. Scan rate: 50 mV s^{-1}.
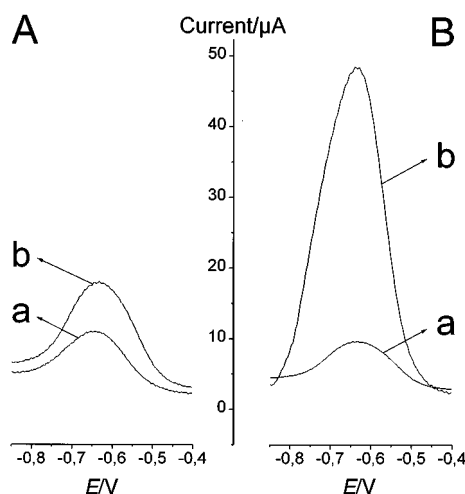

Fig. 2 Square wave voltammograms for 1.0×10^{-6} M paraquat at carbon paste (A) and screen-printed carbon (B) electrodes, recorded after 30 min soaking in solution, with a 100 Hz frequency, a 5 mV step height and a 50 mV modulation amplitude; (a) bare electrodes, (b) 10% zeolite Y-modified electrodes. Supporting electrolyte: 0.1 M NaCl.

Table 1 Cyclic voltammetry characteristics observed after soaking the electrodes for 2 h (under nitrogen bubbling) in 2.0×10^{-4} M PQ^{2+} (+0.1 M NaCl); scan rate: 50 mV s^{-1}

Electrode	First electron transfer[a]			Second electron transfer[b]		
	E_{C1}/V	E_{A1}/V	i_{C1}/i_{A1}	E_{C2}/V	E_{C2}/V	i_{C2}/i_{A2}[c]
Bare CPE	-0.69	-0.63	0.99	-0.99	-0.91	1.1
Bare SPE	-0.68	-0.62	1.00	-1.01	-0.94	0.75
Zeolite-modified CPE	-0.71	-0.62	0.98	-0.97	-0.89	1.8
Zeolite-modified SPE	-0.70	-0.61	0.96	-1.01	-0.87	2.3

[a] Potential scan ranging from -0.30 V to -0.85 V. [b] Potential scan ranging from -0.30 V to -1.30 V. [c] Peak currents were calculated by estimation of background currents after the first peak.

faster desorption of paraquat after 5 min accumulation from a 1.0×10^{-6} M solution: 30 min soaking in 0.1 M NaCl resulted in fractions ranging from 4 to 11% of the analyte left in the electrode, depending on the zeolite loading (Fig. 3). This could be rationalised by considering the different nature of the electrodes: thin-layer for SPZME which does not allow the solution to diffuse deeply in the bulk electrode, and bulky for ZMCPE which contributes to significant imbibition of the paste interior by the external solution. The release efficiency is concentration dependent, and at 1.0×10^{-7} M PQ^{2+} total desorption was observed with SPZMEs in less than 15 min while maintaining a 55% signal with ZMCPE.

The nature of the zeolite-modified electrode was also found to affect the kinetics of the accumulation process (Fig. 4). In all cases, the signal increased with increasing the accumulation period; a faster response time was obtained with using SPZMEs as compared to ZMCPE. SPZMEs yielded 90% of the maximum signal within 5 min, while carbon paste required more than one hour to reach the equilibrium. Once again this behaviour can be attributed to the thin layer structure of SPZMEs preventing them from any significant diffusion of the solution in the bulk of the electrode. Surprisingly, the voltammetric response was not found to rise upon increasing the zeolite content in the screen-printed electrode, contrary to what one would expect from previous work dealing with electrochemical sensors based on chemically modified electrodes. A possible explanation for this could be found in the lower real electrode surface area upon increasing the zeolite content in the
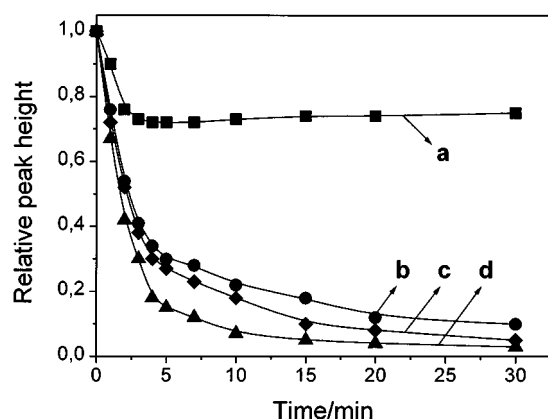

Fig. 3 Relative peak current response for release of 1.0×10^{-6} M paraquat from several modified electrodes into 0.1 M NaCl: 10% zeolite-modified carbon paste electrode (a), and screen-printed carbon electrodes modified with 5% (b), 10% (c), and 15% (d) zeolite Y. Other conditions as in Fig. 2.

Fig. 4 Peak current response for the uptake of 1.0×10^{-6} M paraquat in the modified electrodes (as monitored by square wave voltammetry): 10% zeolite-modified carbon paste electrode (a), and screen-printed carbon electrodes modified with 5% (b), 10% (c), and 15% (d) zeolite Y. Other conditions as in Fig. 2.
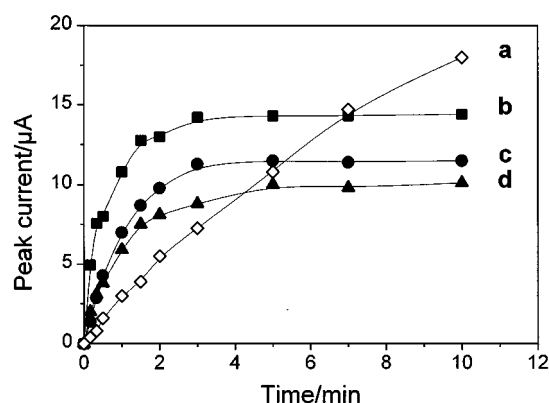
carbon ink. Indeed, back-diffusion scanning electron micrographs of SPZMEs containing either 5 or 15% zeolite have revealed a significantly larger occupation of the electrode surface by zeolites in the last case. As a consequence, if a higher amount of zeolite is thought to lead to higher accumulation efficiency, the detection of these species could be somewhat limited by the lower available carbon on the strip surface.

Determination of paraquat and diquat at screen-printed electrodes modified with zeolite Y. Square wave voltammograms were recorded at SPZMEs, respectively immersed in the electrolyte solution before carrying out the accumulation step (multiple analysis with the same strip) and untreated (single use electrode), for various concentrations of both PQ^{2+} and DQ^{2+}. The results indicate linear calibrations between 1×10^{-6} M and 1×10^{-5} M for both herbicides, but a higher sensitivity (2.5 times) was observed for single use SPZMEs compared to that obtained after soaking the electrodes in the electrolyte solution before the analyte accumulation. This might be attributed to favoured ion exchange of the analyte in the absence of electrolyte cations. It is noteworthy that this decrease in sensitivity was not observed when soaking the electrode in solutions containing less than 10^{-3} M metal cations. The proposed sensor could be used in case of accidental dissemination of these herbicides in aqueous environments.

Selective uptake of paraquat over diquat by zeolite ZSM-5

Paraquat and diquat have very similar electrochemical behaviour so that their voltammetric distinction from each other remains impossible. Moreover the selective accumulation of one of these species in the presence of the other has still to be demonstrated. By considering the different sizes of these herbicides and the possibility for zeolites to accumulate cations by ion exchange and, in the same time, to discriminate between their size, the idea arose to find a zeolite liable to accumulate paraquat while excluding diquat. It is known that entrance to the zeolite framework is usually governed by the size of rings involving 6, 8, 10, or 12 oxygen atoms linked together by either silicon or aluminium atoms.[31] In the zeolite A structure, the main aperture is formed by an 8-oxygen ring which does not allow diffusion of species larger than 4–5 Å; indeed, electrodes modified with this zeolite did not display any preconcentration behaviour towards paraquat.[20,32] On the other hand, zeolite Y to which the entrance is controlled by a 12-oxygen ring (~ 8 Å) is able to accumulate both paraquat and diquat by ion exchange, and this has been exploited for the voltammetric determination of these species (Fig. 5). Therefore, a zeolite structure displaying pore apertures defined by 10-oxygen rings should be promising for the differentiation between PQ^{2+} and DQ^{2+}.
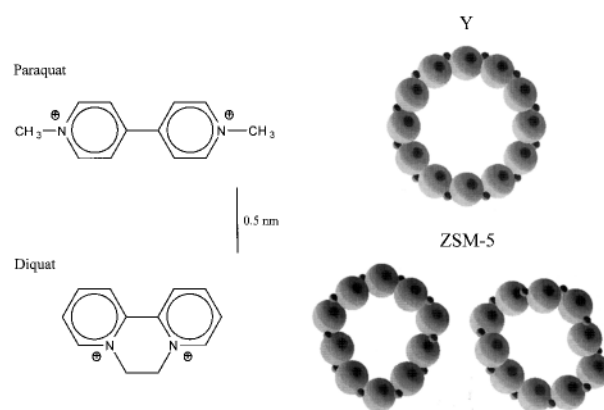

Fig. 5 Structures of paraquat (PQ^{2+}) and diquat (DQ^{2+}) compared to the 12-oxygen ring entrance to zeolite Y (face 111) and the 10-oxygen ring entrances (faces 010 and 100) to zeolite ZSM-5.

Table 2 Distribution of paraquat (PQ²⁺) and diquat (DQ²⁺) between solution and zeolite phases as a function of the zeolite type

Initial conditions in solution[a]		Composition of zeolites at the equilibrium[b]			
PQ²⁺ added/ mM	DQ²⁺ added/ mM	PQ²⁺ in Y/ mmol g⁻¹	DQ²⁺ in Y/ mmol g⁻¹	PQ²⁺ in ZSM-5/ mmol g⁻¹	DQ²⁺ in ZSM-5/ mmol g⁻¹
0.10	—	0.33	—	0.32	—
0.20	—	0.67	—	0.36	—
0.30	—	0.98	—	0.37	—
—	0.10	—	0.32	—	< 0.005[c]
—	0.20	—	0.57	—	< 0.005[c]
—	0.30	—	0.81	—	< 0.005[c]
0.05	0.05	0.16	0.17	0.15	< 0.005[c]
0.10	0.10	0.29	0.33	0.29	< 0.005[c]
0.15	0.15	0.43	0.50	0.35	< 0.005[c]

[a] Slurry: 10 mg zeolite in 30 ml solution. [b] Calculated from the measured residual concentration of PQ²⁺ and DQ²⁺ in solution after equilibration. [c] Lowest measurable value.

Zeolite ZSM-5 offers this specification.[33–35] In ZSM-5, the 10-oxygen rings are distorted two different degrees, defining a tridimensional lattice made of right and zigzag channels sizing respectively 5.3 × 5.6 Å and 5.1 × 5.5 Å. Fig. 5 illustrates the possibility for selective accumulation, showing that both PQ²⁺ and DQ²⁺ can readily enter the 12-oxygen ring of zeolite Y while only PQ²⁺ species could be accommodated within the channels of ZSM-5, DQ²⁺ being excluded because of its larger size.

The hypothesis has been checked and results are presented in Table 2, indicating clearly the selective accumulation of PQ²⁺ over DQ²⁺ in ZSM-5. Whether alone or in the presence of DQ²⁺, PQ²⁺ is incorporated within the ZSM-5 structure at the same level (up to about 0.37 mmol g⁻¹) while DQ²⁺ is totally excluded from the internal ZSM-5 channels. By comparison, both herbicides are readily incorporated to a large extent (0.98 for PQ²⁺, and 0.81 for DQ²⁺) in the supercages of zeolite Y; when used in mixture, a slight preference for DQ²⁺ was observed, most probably because of favourable charge distribution in the zeolite framework. Another feature of the results of Table 2 is the high affinity of zeolites for PQ²⁺ and DQ²⁺ species (Y for both these herbicides, and ZSM-5 for PQ²⁺): when the initial concentration of the analytes was less than that corresponding to the saturation of the accessible ion exchange sites, all of them (macroscopically) were incorporated into the aluminosilicate with a concomitant leaching of equivalent concentrations of sodium ions in the solution.

While the accumulation of PQ²⁺ and DQ²⁺ in zeolite Y can be exploited for their voltammetric quantification after back ion exchange with the electrolyte cation (Na⁺), by using zeolite-modified electrodes, the selective accumulation of PQ²⁺ in ZSM-5 was not appropriate to the sensor field because desorption was not possible. Indeed, the interactions between PQ²⁺ and ZSM-5 were so strong that no desorption occurred even under severe experimental conditions. No desorption was observed in high ionic strength medium (6 M NaCl), in concentrated acid (1 M HNO₃ or HCl) or basic (1 M NaOH) solutions, in organic solvents (acetonitrile or dimethylsulfoxide), or even in the presence of an ion pairing agent for PQ²⁺ species (0.1 M sodium dodecylsulfate). Accordingly, no voltammetric signal was observed in these media for PQ²⁺ after accumulation at ZSM-5-modified (either carbon paste or screen-printed) electrodes. Sodium dithionite, known to reduce PQ²⁺ into the corresponding blue radical cation, was also tested and resulted in the blue coloration of zeolite particles, but no significant leaching of paraquat species in solution was observed. This indicates a very strong binding of this toxic herbicide to ZSM-5 which is most probably due to confinement effects in the sorption process[36] because of the very similar size of PQ²⁺ compared to that of the zeolite channels. This makes zeolite ZSM-5 a promising sorbent for the treatment of solutions infected by this herbicide.

Conclusions

We have demonstrated that screen-printing technology allowed the preparation of new types of zeolite-modified electrodes, which are promising for the mass production of low-cost and single-use zeolite-based sensors, with significant advantages (faster response time and easier chemical regeneration) compared to the corresponding zeolite-modified carbon paste electrodes. Using the herbicides paraquat and diquat as representative electroactive probes, it was shown that the screen-printed carbon electrodes modified with zeolite Y were characterised by restricted diffusion of the solution in the bulk of the electrode, which is known to be a serious limitation in the use of zeolite-modified carbon paste electrodes for electroanalysis. In addition, the use of zeolite ZSM-5 resulted in the selective accumulation of paraquat over diquat. The interactions of this herbicide with the aluminosilicate framework were so strong that desorption was prevented in a wide range of experimental conditions, making ZSM-5 a good substrate for the irreversible uptake of this toxic species. Future applications of screen-printed zeolite-modified electrodes, particularly on-site field screening, would require dual-electrode strips, with a printed reference electrode along the working one.

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