Paraquat and Diquat Sorption on Iron Oxide Coated Quartz Particles and the Effect of Phosphates

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The covering of quartz particles (Q) with Fe oxides provides high capacity sorption and immobilization of both paraquat (PQ) and diquat (DQ) as well as phosphates (P), that can be used to remediate contaminated environments due to their persistence. Both PQ and DQ have higher sorption strength on crystalline iron oxide coated quartz particles (Q_{Fec}) than on amorphous iron oxides (Q_{Fea}), but the highest is for PQ, which might be due to its strongest interaction. The increasing addition of P contributes to the increase of quat maximum sorption on iron oxide coated quartz particles, because the cosorption of P causes the surface charge to become more negative, facilitating the sorption of positively charged quats, but this happens in a different way for both quats. It was also seen that the formation of phosphate−quat complexes has a lower affinity than P by the coated quartz particles. The characteristics of the coated quartz particles would allow increased sorption of these quaternary ammonium herbicide contaminants.

1. Introduction

Soil sorption of bipyridylium herbicides (largely paraquat, PQ, and diquat, DQ; Table 1) has revealed that both are strongly adsorbed by soils and soil clays.[1] Also, according to Calderbank,[2] some clays in soil dramatically reduce the herbicidal power of both compounds. More recent studies have shown that these herbicides have a high affinity for clay surfaces in relation to soil organic matter, especially as compared to inorganic cations.[3−7] Their interactions with clay particles depend on the particular type of clay. Thus, Weber and Scott[8] found PQ to bind to interlayer spacings in montmorillonites via Coulombic and van der Waals forces and also to kaolinite via Coulombic forces alone. The widespread use of bipyridylium herbicides in agricultural applications such as preharvest nonselective weed control means that these compounds may be present as residues in surface water (which are supplied as drinking water) owing to their persistence and polar character.[9] On the other hand, phosphorus speciation and mobility is controlled by surface reactions; in soils, the importance of iron oxide coatings on other soil minerals in controlling phosphate (P) solubility and sorption has been recognized.[10] Phosphate is considered to sorb mainly as an inner-sphere complex which means that the sorption takes place at specific coordination sites on the oxides or hydroxides and no water molecules are present between the surface and the phosphate ion. Phosphorus sorption is a continuous sequence of sorption and precipitation and consists of two processes, one relatively fast, reversible sorption process and the other relatively slow, practically irreversible precipitation-like process, and it is very difficult to distinguish between the two.[11]

This work is a new approach in an ongoing research project intended to increase available knowledge about the specific factors affecting sorption processes, and hence mobility, of contaminants by soil components.[12−16] The original aim of the study was to investigate the effect of Fe oxides precipitated in quartz particles, on paraquat, diquat, and phosphorus sorption, using batch experiments, and understand the role of their interactions on their sorption.

2. Material and Methods

2.1. Quartz and Quartz Iron Oxides. The quartz (Q) particles used in this study came from an opencast quartz mine under exploitation in the northwest of Spain (Pico Sacro, Boqueixón, A Coruña). The particles were obtained by grinding the quartz material and the fraction < 100 μm was selected. On the selected particles iron oxides were precipitated following the procedure described by Arias et al.;[17] in short the method is as follows: 100 mL of a 0.4 M solution of $FeNO_3$ was added to 50 g of quartz and made up to 200 mL with distilled−deionized water. Subsequently, 30 % ammonia solution was added until the pH of the suspension reached 7.5; then, the solids were separated and washed with distilled water until the washings showed a negative response to Nessler's reagent. Finally, the solids were oven-dried at 40 °C until they had a constant weight. Two types of samples were obtained with 4.5 % Fe: samples coated with crystalline iron oxides (Q_{Fec}) and those coated with amorphous iron oxides (Q_{Fea}); crystallization was favored by, following washing as before, suspending the samples in 500 mL of water and maintaining them at 70 °C for 17 days before oven-drying at 40 °C (aging process). The noncrystalline/amorphous Fe can be evaluated by extraction with oxalic acid/oxalate (Fe_o). The total Fe noninvolved in the formation of silicates can be obtained by extraction with dithionite/citrate (Fe_d), that is, both the crystalline and the noncrystalline Fe. The value of the Fe_o/Fe_d ratio for Q_{Fea} particles (those nonaged) is bigger than the value

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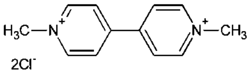
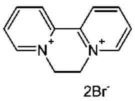
Table 1. Characteristics of the Quaternary Herbicides Studied

Common name	PQ	DQ
Chemical structure		
Name	1,1'-dimethyl-4,4'-bipyridylium dichloride	1,1'-Ethylene-2,2'-bipyridylium dibromide
CAS n°.	1910-42-5	85-00-7
MW [a]	257.2 (cation= 186)	344 (cation= 184)
S[b] (g/L)	620	677
log Pow[c]	–4.5	–4.6
Koc [d]	15 to 51	164 to 134
Soil half-life[e]	644	3450

[a] Molecular weight. [b] Solubility in water at 20 °C. [c] Octanol−water partition coefficient at 20 °C. [d] Partition coefficient normalized to organic carbon content ($mL\cdot g_{oc}^{-1}$ or $L\cdot kg_{oc}^{-1}$). [e] Aerobic soil half-life (avg, days).

Table 2. Sample Characteristics

	particle size distribution (%)					$S_{(EGME)}$
sample	< 2 μm	(2 to 20) μm	(20 to 50) μm	(50 to 100) μm	> 100 μm	$m^2\cdot g^{-1}$
Q	4.2	24.2	52.3	19.3	0.0	3
Q_{Fea}	1.4	5.9	66.6	25.0	1.1	50
Q_{Fec}	1.6	8.9	65.0	17.5	7.0	28

found for Q_{Fec} particles (those aged). The value of the Fe_o/Fe_d ratio (Q_{Fea}) is 1.0. This result implies that all of the iron present in the particles is noncrystalline. The value of the Fe_o/Fe_d ratio (Q_{Fec}) is 0.6 (approximately half of iron is crystalline). This result proves that crystalline Fe increases on increasing the aging of the particles. The iron present in the Q_{Fea} particles is in the form of oxides, Fe_2O_3, while the Q_{Fec} show a typical X-ray diffraction pattern of hematite (α-Fe_2O_3) (reflections at (2.69 and 2.51) Å); this has already been described in-depth by us.[17]

Particle size distribution was measured following the method described: 5 g of sample was suspended in 25 mL of distilled−deionized water and shaken end-overend (4 h); then, the particle size-fractions > 50 μm were determined by wet sieving and those ≤ 50 μm by the Robinson pipet method. The equivalent spherical diameter intervals obtained are listed in Table 2. To determine the specific surface area ($S_{(EGME)}$), an ethylene glycol monoethyl ether (EGME) sorption test has been carried out, and results are shown for samples in Table 2. The point of zero charge (ZPC) was also determined using potentiometric titrations at low ionic strength. The ZPC remains constant for Q_{Fe} independent of the age of the particles and hence of their crystallinity (8.0 in both cases).

2.2. Contaminant Sorption by a Batch Equilibrium Technique. Quat sorption was determined by using a batch equilibrium technique, and all chemicals used were of analytical grade. A sample of particles (50 mg) was mixed with 10 mL of a 0.01 M solution of $CaCl_2$ with any of the quats at concentrations between (10 and 160) μM; this range was selected on the basis of quats detection in solution after equilibration due to their high sorption onto the material. The suspensions were kept at a constant temperature of (20 ± 2) °C and thoroughly agitated in an orbital shaker at 200 rpm for 24 h (in good agreement with our previous studies by Pateiro-Moure et al.[12−16]), and then the aqueous solution was separated by centrifugation at 4000 rpm for 15 min for subsequent spectrophotometric determination of PQ (at 258 nm) or DQ (at 310 nm) and pH measurement. All determinations were conducted in triplicate, and the method relative standard deviations were lower than 5 %. Quat recoveries ranged from 98 % to 100 % after separation of the aqueous solution by centrifugation with estimated quantification limits between (5 and 10) nM.

Experimental data (9 to 10 points) were fitted to Langmuir's eq 1 and Freundlich's eq 2 using the Levenberg−Marquardt algorithm.

$$Q_e = \frac{K_L C_e X_m}{1 + K_L C_e} \qquad (1)$$

where Q_e is the amount adsorbed per mass unit, K_L is a constant related to the sorption process, X_m is the maximum sorption capacity, and C_e is the equilibrium concentration.

$$Q_e = K_F C_e^{1/n} \qquad (2)$$

where K_F and $1/n$ are two constants.

The influence of phosphates on paraquat and diquat sorption was performed by fixing the quat concentration at 3.0 $mg\cdot L^{-1}$ (16 mM) while ranging P concentration between (0 and 45) $mg\cdot L^{-1}$ [(0, 4, 7, 14, 30, and 45) $mg\cdot L^{-1}$; (42 to 474) mM] in the background solution of $CaCl_2$. Instead, the influence of

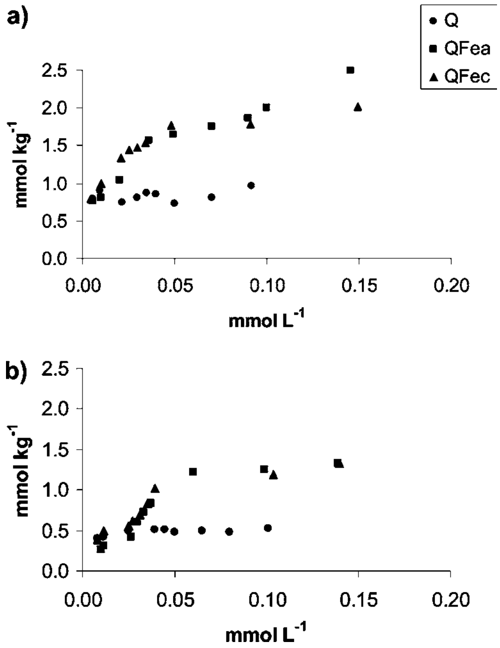


Figure 1. Sorption curves: (a) paraquat and (b) diquat.

paraquat and diquat on phosphate sorption was performed at P concentrations of (10 and 15) mg$\cdot$L^{-1} [(105 and 158) μM] keeping the quat concentration constant at 3.0 mg$\cdot$L^{-1} (16 mM) in the background solution. Phosphorus sorption was determined using a batch equilibrium technique. The phosphorus was added as KH_2PO_4 to 50 mg of sample mixed with 10 mL of a 0.01 M solution of $CaCl_2$ as a background electrolyte. Samples were shaken at (20 ± 2) °C throughout the equilibration period (24 h), after which they were centrifuged at 4000 rpm for 15 min. The solution was used to measure the pH and to determine P, as applicable, by the colorimetric ascorbic acid method. All determinations were conducted in triplicate, and the method relative standard deviations were lower than 5 %.

Data were subjected to a one-way analysis of variance with treatment as a fixed factor. Whenever significant differences were detected at the 0.05 level, the means were separated by Duncan's multiple range test in groups coded by "a" and "b". All analyses were performed with the Statgraphics statistical software.

3. Results and Discussion

3.1. Paraquat and Diquat Sorption on Iron Oxide Coated Quartz Particles. A high sorption of quats on Q_{Fea} and Q_{Fec} took place. The experimental sorption isotherms obtained for quats on both adsorbents may be classified as L-type in the Giles classification (Figure 1). In general, better fits were obtained from the Langmuir rather than the Freundlich equation. The curves tend to define a plateau suggesting the formation of a complete monolayer of quat molecules covering the adsorbent surface (isotherms belonging to subgroup II of the Giles classification). The cationic nature of quats governs its behavior, so the main sorption mechanism is a strong electrostatic interaction with the negatively charged surface of the adsorbents.[18,19]

For both quats, on increasing crystallinity, an increase in sorption strength (K_L) but a decrease in sorption maximum capacity (X_m) was found (Table 3). Both PQ and DQ have higher sorption strength (K_L) on crystalline iron oxide coated quartz particles than on amorphous ones [(99 and 30) L$\cdot$mmol^{-1} on Q_{Fec} versus (41 and 16) L$\cdot$mmol^{-1} on Q_{Fea} for PQ and DQ, respectively], but the highest is for PQ [(99 or 41) L$\cdot$mmol^{-1}], which might be due to its strongest sorption strength. The maximum sorption capacity (X_m) for both quats can be found, instead, on amorphous iron-oxides coated quartz particles [(2.6 and 2.0) mmol$\cdot$kg^{-1} on Q_{Fea} vs (2.1 and 1.6) mmol$\cdot$kg^{-1} on Q_{Fec} for PQ and DQ, respectively] due to their larger specific surface ($S_{(EGME)}$ is 50 for Q_{Fea} vs 28 for Q_{Fec}). Anyway, expressing X_m as a function of the specific surface (nmol$\cdot$m^{-2}), the situation reverts in favor of Q_{Fec} [(52 and 40) nmol$\cdot$m^{-2} for Q_{Fea} vs (75 and 57) nmol$\cdot$m^{-2} for Q_{Fec} for PQ and DQ, respectively]. PQ has the largest sorption capacity in both materials with regards to DQ, which is in good consonance with its also largest sorption strength in any of the materials [K_L = (41 and 99) L$\cdot$mmol^{-1} for Q_{Fea} and Q_{Fec}, respectively]. Anyway, $S_{(EGME)}$ (50 for Q_{Fea} vs 28 for Q_{Fec}) has the strongest effect on maximum sorption.

Diffuse contaminant emissions usually originate from the drainage of agricultural land and from groundwater flow into surface waters. By increasing the sorption of contaminants (such as quat-based drying herbicides) by soil colloids (such as iron (Fe) oxides) via Coulombic and/or van der Waals forces,[8] it might induce the regeneration of contaminated waters.

3.2. Interaction between Phosphates and Quats (Paraquat and Diquat). Phosphorus and quats could coincide in agricultural soils since phosphorus is applied as fertilizer and quats as drying herbicides. The sorption of P makes the surface charge of its sorbents more negative,[20] giving rise to more negative zeta potentials. Thus, the originally positive surface charge of iron (Fe) oxides can become negative as a consequence of P sorption.[20] It still remains unclear to what extent the sorption of P causes the retention of other contaminants, such as the quaternary ammonium herbicides, in oxide-coated particles of quartz sand.

The higher addition of phosphates (P) contributes to the increase of quat maximum sorption on iron oxide coated quartz particles (Q_{Fe}) (Table 4). This is because the cosorption of P causes the surface charge to become more negative, facilitating the sorption of positively charged quats, but in a different way for both quats. The interaction between both Q_{Fe} and P is mainly electrostatic. For PQ, the effect of increased sorption % by P is similar for both amorphous and crystalline iron oxide coated quartz particles (70 % vs the slightly lower 65 % increase at 3.0 mg$\cdot$L^{-1} for a P concentration of 45 mg$\cdot$L^{-1}). This can be attributed to P increasing the PQ sorption strength (K_L) in the same % ratio for both systems independently of their different K_L (99 L$\cdot$mmol^{-1} on Q_{Fec} vs 41 L$\cdot$mmol^{-1} on Q_{Fea}). For DQ, instead, the higher effect of increased sorption by P takes place with the amorphous iron oxide coated quartz particles (104 % vs 45 % increase at 3.0 mg$\cdot$L^{-1} for a P concentration of 45 mg$\cdot$L^{-1}). It seems that, for DQ, the key control parameter, reinforced by P addition, is still $S_{(EGME)}$ (50 for Q_{Fea} vs 28 for Q_{Fec}). The results allow P to be used as a modification of the studied adsorbent in aqueous media to remove quat-based contaminants, since it contributes to govern quat retention.

The sorption of P on Q_{Fea} and Q_{Fec} particles was favored. A decrease in the P sorption on an increasing degree of crystallinity of the coated material was found (Table 5). The addition of quats to a suspension of iron oxide coated quartz particles contributes to a decrease in P sorption (decrease of (40 to 73) %). This can be explained by the formation of a P-quat complexes having a lower affinity than P by the coated quartz particles. The highest decrease in P sorption was reached when PQ is added to the coated quartz particles + P suspension (decrease of (60 and 73) % for Q_{Fea} and Q_{Fec}, respectively).

Table 3. Langmuir and Freundlich Equation Parameters (Average ± Standard Deviation, Obtained with 9 or 10 Experimental Points): Adsorbed, in mmol·kg^{-1}, versus Equilibrium Concentrations, in mmol·L^{-1}

sample		Langmuir equation				Freundlich equation		
		K_L (L·mmol^{-1})	X_m (mmol·kg^{-1})	X_m (nmol·m^{-2})	R^2	K_F	$1/n$	R^2
Q	PQ	--[c]	--	--	--	--	--	--
	DQ	--	--	--	--	--	--	--
Q_{Fea}	PQ	41 ± 11^a	2.6 ± 0.2^a	52	0.911	5.0 ± 0.4^a	0.38 ± 0.03^a	0.970
	DQ	16 ± 5^b	2.0 ± 0.3^b	40	0.927	4.0 ± 1.0^a	0.54 ± 0.08^a	0.878
Q_{Fec}	PQ	99 ± 13^a	2.1 ± 0.1^a	75	0.961	3.3 ± 0.3^a	0.24 ± 0.02^b	0.935
	DQ	30 ± 7^b	1.6 ± 0.2^b	57	0.910	3.0 ± 0.4^a	0.40 ± 0.05^a	0.915

[a,b] Whenever significant differences were detected at the 0.05 level, the means were separated by Duncan's multiple range test in groups coded by "a" and "b" [c] --: constant background sorption.

Table 4. Influence of Increasing P Concentration in Paraquat and Diquat % Sorption Increase at 3.0 mg·L^{-1} (0.016 mmol·L^{-1}) Compared to Zero P Addition[a]

	[P] mmol·L^{-1} (mg·L^{-1})	P + PQ (PQ % increase)	P + DQ (DQ % increase)
Q_{Fea}	0	0	0
	0.042 (4)	22 ± 1.1	31 ± 1.5
	0.074 (7)	26 ± 1.3	67 ± 3.3
	0.147 (14)	44 ± 2.0	81 ± 3.9
	0.316 (30)	54 ± 2.5	95 ± 4.5
	0.474 (45)	70 ± 3.2	104 ± 5.1
Q_{Fec}	0	0	0
	0.042 (4)	12 ± 0.5	8 ± 0.4
	0.074 (7)	20 ± 0.9	15 ± 0.8
	0.147 (14)	33 ± 1.5	28 ± 1.4
	0.316 (30)	45 ± 2.2	32 ± 1.5
	0.474 (45)	65 ± 3.1	45 ± 2.3

[a] Relative standard deviations were lower than 5 % ($n = 3$).

Table 5. Influence of Paraquat and Diquat in P Sorption at Two Levels [(0.105 and 0.158) mmol·L^{-1} or (10 and 15) mg·L^{-1}][a]

		decrease of phosphate sorption on quartz particles (%)	
	[P] mmol·L^{-1} (mg·L^{-1})	with PQ	with DQ
Q_{Fea}	0.105 (10)	53 ± 2.7	47 ± 2.2
	0.158 (15)	60 ± 3.1	45 ± 2.2
Q_{Fec}	0.105 (10)	60 ± 3.0	40 ± 2.1
	0.158 (15)	73 ± 3.7	40 ± 1.9

[a] Relative standard deviations were lower than 5 % ($n = 3$).

This evidence makes clear than the interaction PQ-P is higher than that of DQ-P and has a larger effect for coated quartz particles with lower $S_{(EGME)}$. The decreasing effect of DQ on maximum P sorption on coated quartz particles (decrease of (47 and 40) % for Q_{Fea} and Q_{Fec}, respectively) was, instead, higher in the case of Q_{Fea}. This is to say that the decreasing effect of DQ on P sorption is lower on crystalline iron oxide coated quartz particles due to the lower affinity of the DQ-P complexes versus amorphous iron oxide coated quartz particles.

Herbicide pollution in crop soils is usually produced by their application inputs, being the producer responsible for such an action.[12] Weeds in the field are regularly covered with dust to some extent. The applied herbicide binds to dust particles, thus becoming inactivated. Because of such inactivation, growers have to increase the rates used to obtain efficient weed control. This increases considerably the levels of herbicides applied.

This work helps to cover some of the research needs in the area of herbicide residues in soils: studying the factors controlling their mobility seems to be a substantial contemporary issue to guarantee environmental quality. While the effect of P adsorption on the surface charge and colloidal stability of suspensions has received considerable attention, it was necessary to know to what extent the sorption of P causes the retention of other contaminants, such as the quaternary ammonium herbicides, in oxide-coated particles of quartz sand. Phosphorus sorption seems to be a continuous sequence of adsorption and precipitation and consists of two processes, and it is very difficult to distinguish between the two.[11]

4. Conclusions

The covering of quartz particles with Fe oxides provides a high capacity sorption and immobilization of quats, which was increased by phosphates. The sorption process has been described by Freundlich and Langmuir isotherms. In general the Langmuir equation yields better fits than the Freundlich equation. The maximum sorption capacity (X_m) for both quats can be found on amorphous iron oxide coated quartz particles [(2.6 and 2.0) mmol·kg^{-1} for Q_{Fea} vs (2.1 and 1.6) mmol·kg^{-1} for Q_{Fec} for PQ and DQ, respectively] due to their largest specific surface ($S_{(EGME)}$ is 50 for Q_{Fea} vs 28 for Q_{Fec}). The increasing addition of phosphates (P) contributes to the increase of quat maximum sorption on iron oxide coated quartz particles, probably because the cosorption of P causes the surface charge to become more negative, facilitating the sorption of positively charged quats.

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