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Adsorption of nitrogen heterocyclic compounds (NHC) on soil minerals: Quinoline as an example


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KEYWORDS: water treatment, contaminant remediation, municipal waste leachate, organic contamination.
Understanding the adsorption behavior of nitrogen heterocyclic compounds (NHCs) on soil minerals underlies more effective design of wastewater treatment and soil/groundwater remediation. We investigated adsorption of quinoline, a representative NHC, on quartz sand (using Berea sandstone as a model), at 3<pH<9, in low (0.05 M) and high (0.7 M) ionic strength solutions where NaCl was the background electrolyte. Minor clay (kaolinite) in the sandstone contributed significantly to quinoline uptake. Adsorption peaked at pH~6. It decreased from 2 equivalent monolayers at low ionic strength to a monolayer at NaCl activity approaching that of seawater. A triple layer surface complexation model fits the data well, where quartz and kaolinite contributed sites for three types of quinoline (Q) complexes: 1) innersphere ≡SiOHQ; 2) outersphere ≡SiOHQH+ and 3) innersphere ≡AlOHQ2. Aluminol kaolinite sites promote multilayer quinoline adsorption, whereas only monolayers form on silanol sites. Site density calculations and molecular dynamics (MD) confirmed that quinoline adsorbs upright, on edge, and multilayer adsorption follows formation of the initial monolayer. Our results confirm the effectiveness of sand(stones) and clays for removing NHCs from waste and groundwaters.

1. Introduction

Nitrogen bearing heterocyclic compounds (NHCs), as well as sulfur and oxygen compounds, are often found as contaminants in municipal waste leachate and groundwater in the vicinity of hydrocarbon production [1, 2], storage and spills [3-6]. Organic molecule shape and functional group composition determine extent of uptake and this controls the properties of mineral surfaces [7, 8]. Quinoline (Table 1) and its derivatives [9] are examples of NHCs [10] that can participate in reactions typical for benzene and pyridine [11], are highly soluble in water and of interest
because they increase cancer risk [10]. Research is reported on quinoline biodegradation [12] by microorganisms [13-15] and removal by activated carbon [16-19], mesoporous alumino-silicates [20, 21], metal oxides [22] and metal-organic frameworks [23, 24], but little is known about the mechanisms of quinoline adsorption on natural materials such as clays, quartz, carbonate minerals and soils [25] in general, which limits the effectiveness of remediation strategies.

Table 1. Structure and properties of quinoline.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Molar mass, g/mol</th>
<th>Chemical Structure</th>
<th>Density, g/cm³</th>
<th>Melting/Boiling point, °C</th>
<th>Solubility in water [26], mM</th>
<th>pKa</th>
<th>LD₅₀ [27], mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoline (1-azanaphthalene)</td>
<td>C₉H₇N</td>
<td>129</td>
<td></td>
<td>1.09</td>
<td>-15/237</td>
<td>47</td>
<td>4.93</td>
<td>331</td>
</tr>
</tbody>
</table>

Quinoline is an organic base (pKₐ 4.93) and its adsorption is pH dependent. Adsorption on clays (Na⁺, NH₄⁺, K⁺, Ca²⁺-montmorillonites, Na,K-kaolinites) and several oxides (SiO₂, Al₂O₃, Fe₂O₃) is maximum at pH ~6.0 [28]. At lower pH, decreased adsorption results from proton competition with quinolinium. At higher pH, mineral surfaces are negatively charged, so binding of quinoline is less favorable. On amorphous silica, maximum adsorption is reported at lower pH, close to quinoline pKₐ [29].

Many have argued that cation exchange is the main adsorption mechanism for protonated quinoline [30-32] but surface complexation of the neutral species and partitioning onto soil organic carbon are other explanations [33]. Studies of surfactant modified clays [34], Na-montmorillonite
[35-37], Ca-montmorillonite [36-39], smectite [37], illite [36] and kaolinite [36, 38, 40] have shown that at pH>pKₐ, adsorption of quinoline neutral species dominates [41]. For materials with low organic carbon, such as subsoils, even at 2 pH units above the pKₐ, protonated quinoline species still exist [42]. This was explained by enhanced protonation close to the mineral surface. For fibrous silicates (sepiolite, palygorskite) and saponite, minor quinoline was observed to exchange [43] with Na⁺.

The presence of cations, such as Mg²⁺, Ca²⁺, Na⁺, K⁺ and NH₄⁺, has a significant effect on adsorption through quinoline-metal ion complexing, whereas anions, SO₄²⁻ and Cl⁻, have little or no effect. Cation adsorption on combusted Rundle shale increased in the order Mg²⁺≥Ca²⁺>NH₄⁺>Na⁺≥K⁺, indicating that cation exchange with protonated quinoline is not the only mechanism; quinoline also adsorbs in coordination with metal cations [44]. The lack of correlation between the amount of adsorbed quinoline and cation exchange capacity was also observed for clayey till [45] and was explained by the strength of quinoline-cation bonding. When present in oil, NHCs change porous medium wettability, whether in oil reservoirs or groundwater aquifers. Evolution of grain surfaces from water wet to oil wet enhances uptake of other organic compounds [46]. It is known that quinoline promotes sorption of pyrene on smectites [47] and 5-indanol on kaolinite [48]. Quinoline participates in competitive adsorption from binary mixtures with pyridine and acridine on subsoils [49], and with 1-naphthol and m-cresol on silica gel [50]. Investigations of contact angle on silicate glass and adsorption studies on α-alumina [51] showed that silicate surfaces in the presence of quinoline is independent of salinity but increases with pH. At high pH, quinoline has no influence on wettability, implying minimal adsorption but on α-alumina, adsorption is still significant at high pH, though lower than at neutral or acidic pH.
Our purpose was to investigate quinoline adsorption, as a function of pH and ionic strength on material from a sand aquifer. There is a hypothesis in the oil production community, that hydrocarbons are released more extensively during low salinity injection than by seawater or formation water. Change of salinity for release of contamination is also an interesting concept for remediating soil and aquifers. To test the “low salinity response” hypothesis in the case of quinoline, as a representative of nitrogen containing compounds, we needed a cohesive solid, so we chose Berea sandstone, which is well known to be nearly pure quartz. For experiments requiring powder, we gently crushed some sandstone to separate the grains, while minimizing their fracture. Most sand aquifers contain clay and other minerals but by choosing Berea sandstone, we limited the accessory minerals to kaolinite and trace amounts of mica to facilitate comparison with model minerals and to optimize data analysis. We fit our results with the triple layer surface complexation model (TLM), which can be used over an extended salinity range and it can differentiate between inner and outersphere complexation, to test a common assumption, that organic complexes are outersphere. In the modelling, we differentiated quinoline adsorption between surface silanols, ≡SiOH, and aluminols, ≡AlOH, which will allow further verification if artificial materials containing these functionalities, such as stone wool, can be used for quinoline uptake from wastewater. We used molecular dynamics (MD) simulations, to complement our solution chemistry results and to determine the coordination and orientation of adsorbed quinoline molecules.

2. Experimental

2.1. Materials
The reagents, CaCl$_2$·2H$_2$O, MgCl$_2$·2H$_2$O, KCl and NaCl, were obtained from Sigma-Aldrich, Steinheim, Germany, at ACS purity or higher. Quinoline, Q, supplied by Merck, Darmstadt, Germany (0.004% sulfides) was used as received. We used ultrahigh purity, deionized water with specific resistivity of 18.2 MOhm·cm (MilliQ). For one set of experiments, we made stock solutions with high ionic strength (HIS: 12 mM CaCl$_2$, 58 mM MgCl$_2$, 12 mM KCl, 478 mM NaCl), which has salinity close to seawater (0.7 M; details in Table S1) and low ionic strength (LIS), diluted by a factor of 24. For other experiments, we used buffered solutions of NaCl, at 0.7 and 0.05 M.

The Berea sandstone was cut to make 1×1×0.3 cm$^3$ wafers, for analysis with streaming potential and X-ray photoelectron spectroscopy (XPS). For quinoline adsorption experiments, we used the 125-250 µm sieved fraction from gently crushed sandstone and characterized them for surface area, bulk mineral and surface chemical composition. We also used wafers of quartz (100) and alumina (sapphire) (0001) (MTI Corp.) and powdered γ-alumina from Quantachrome Partikelmesstechnik (QC-SRF-522, #1294, BET SSA 5.22±0.21 m$^2$/g).

2.2. Techniques

X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance (CoK$_\alpha_1$, 1.7902 Å; 2 theta range 5-90; 0.01 °/step and 1 s/step) and compared with the mineral files (ICDD PDF-2 Powder Diffraction File Database) using the Bruker software code, EVA. Pattern-matching and refinement of the crystalline phases was carried out by the Rietveld refinement, with TOPAS[52] to identify and roughly quantify the minerals present. We used an FEI Quanta 3D FEG scanning electron microscope (SEM), in low vacuum (60 Pa), to examine polished thin sections, with a voltage contrast backscattered electron (BSE) detector. An Oxford X-Max system provided energy
**dispersive X-ray spectroscopy** (EDX) (accelerating voltage, 10 kV; beam current, 8 nA, in analytical mode). The sandstone was confirmed to contain quartz, minor clay and trace mica, thus surface sites for adsorption were dominantly silica and alumina.

*Water vapor and nitrogen gas adsorption* were used to determine surface area, using a Quantachrome Autosorb-1 Sorption Analyzer, at 293 K for water and at 77 K for nitrogen in the relative pressure range $0.1<P/P_0<0.3$ ($P_0$, saturated vapor pressure), using the BET (Brunauer, Emmett, Teller) equation [53]. Samples were initially degassed by heating to 200 °C in vacuum ($<10^{-3}$ torr) for 24 hours. The BET plots were linear in the relative pressure range examined and the constant, $C$, was in the interval 50–250, confirming the applicability of the BET equation.

*Elemental analyses* for nitrogen, hydrogen and carbon were made on a Thermo Scientific FLASH 2000 CHN Analyzer. A small amount (7-10 mg) of material was heated in a chamber with high oxygen content at 990 °C to incinerate all organic compounds. Released CO$_2$, H$_2$O and NO$_x$ provided carbon/hydrogen/nitrogen ratios. *Cation exchange capacity* was determined with the single extraction procedure, using 0.25 mol L$^{-1}$ SrCl$_2$ solution to displace exchangeable cations [54].

Surface composition and its change after treatment were determined with *X-ray photoelectron spectra (XPS)*, collected on a Kratos Axis Ultra$^{\text{DLD}}$, using monochromatic Al$_{K\alpha}$ X-rays (hν = 1486.6 eV, power = 150 W). The ultrahigh vacuum (UHV) base pressure was $<5\times10^{-9}$ torr. Pass energy was 160 eV and step size was 0.5 eV for the survey scans. For high resolution of the C1s and N1s regions, we used pass energy of 10 eV and step size of 0.1 eV. We analyzed the data with CasaXPS using Shirley background correction. Spectra were calibrated by assigning the C1s peak
energy to 285 eV. We analyzed both wafer and powdered samples, before and after exposure to solutions. For XPS analyses, survey scans were collected from three different locations.

Zeta potential measurements were made using an Anton Paar SurPass Electrokinetic Analyzer. We used the adjustable gap cell with two 1x1 cm² wafers of Berea sandstone, quartz or alumina. Wafers were placed in the cell, in parallel, separated by ~100 µm. Electrolyte solution (1 mM NaCl) was pushed through the gap between them, with pressure gradually increasing to 300 mbar. pH was controlled with 0.1 M solutions of HCl and NaOH in an autotitrimeter. Zeta potential was determined from 3.0<pH<9.2 and averages were made from 4 measurements at each pH. For wafers, ζ potential was determined from the Helmholtz-Smoluchowski equation:

\[
\zeta = \frac{dI}{dp} \times \eta \times \frac{L}{A},
\]

and for the powders, approximation of Helmholtz-Smoluchowski equation was used:

\[
\zeta = \frac{dU}{dp} \times \eta \times \frac{\kappa_B}{\varepsilon_0} \times \frac{\kappa_B}{\varepsilon_0}
\]

where ζ represents zeta potential; dU/dp and dI/dp, the slope of the streaming potential or current versus pressure; η, electrolyte viscosity; ε₀, vacuum permittivity; ε, dielectric constant of electrolyte; κₘ, specific electric conductivity of the electrolyte outside the capillary system; L, length of the slit channel (10 mm) and A, its cross section. All of these parameters were software controlled and their change during measurement was considered in the ζ potential calculation.

2.3. Procedures
Sample treatment. Berea sandstone was analyzed as powder and wafers, before treatment, to verify the homogeneity of surface composition and after, to monitor changes. We investigated wafers that had been treated for 24 hours in solutions of quinoline at 238 °C, to achieve high uptake. The wafers were dried in ambient conditions and then rinsed with the high (HIS) and low (LIS) salinity solutions for 24 hours. The solution compositions are presented in Table S1. Quartz (100) and alumina (0001) wafers (MTI Corp.), that had been treated in a UV-ozone cleaner for 40 minutes and rinsed with ultradeionized water, were subjected to the same treatment with quinoline, then with HIS or LIS, for comparison.

Quinoline adsorption. The quinoline adsorption experiments were made with crushed sandstone, at room temperature, using NaCl background electrolyte at two ionic strengths, 0.05 M and 0.7 M. The stock solutions contained 40 mM quinoline and 0.05 M Na acetate buffer (0.05 M) at initial pH 3.0, 4.0, 5.0 and 6.0. The solid to liquid ratio was 200 g/L and quinoline concentrations were 1, 5, 10 and 20 mM. Controls contained the buffer solution at the same pH without quinoline. Samples were agitated for 24 hours at 270 rpm, centrifuged at 5000 rpm for 5 minutes and filtered. Pure water at equilibrium with Berea sandstone has pH 8.7 and because the buffer capacity was insufficient, pH changed during the experiments. To track these changes, we measured pH before and after each adsorption experiment. Quinoline uptake was determined by loss from solution, using UV-visible spectroscopy (Perkin Lamda UV-VIS analyzer; peak intensity, 312 nm). Solutions were diluted 20 times to fit the range (0.05 – 1 mM). The quinoline spectrum is pH dependent, so pH was adjusted to acidic by adding 100 µL of 1 M HCl to 900 µL of diluted quinoline solution.

Surface complexation modelling. We used FITEQL 4.0 [55], a computer program that combines a nonlinear least squares fitting with a chemical model to describe aqueous and surface speciation,
to determine the conditional intrinsic equilibrium constants for the various surface complexation equilibria, formulated with the triple layer model (TLM). We assumed the sandstone surface to be composed of \( =\text{SiOH} \) functional groups of quartz and kaolinite and \( =\text{AlOH} \) functional groups of kaolinite. Following Zachara et al. [56], the total site density of kaolinite was assumed to arise from contributions of \( =\text{SiOH} \) (8 nm\(^{-2}\)) [57] and \( =\text{AlOH} \) (6 nm\(^{-2}\)) [56]. Tetrahedral kaolinite sites can carry permanent negative charge, allowing electrostatic interaction with positive ions but this permanent charge is minor in kaolinite. We used solutions of relatively high ionic strength to minimize the effect of adsorption onto the permanently negatively charged sites, that are responsible for the low cation exchange capacity of kaolinite and thus, only the variable charge edge sites are of importance. This means that ionization of \( =\text{SiOH} \) and \( =\text{AlOH} \) control surface charge.

Over the investigated pH region, we expect that \( =\text{SiOH} \) sites deprotonate, while \( =\text{AlOH} \) sites deprotonate or consume protons, depending on pH [58, 59]. Therefore, complex formation and all further reactions of \( =\text{SiOH}^+ \) were not considered. The reactions and constants [56][60][61] for silanol and aluminol, that we used for modelling the adsorption reactions are:

\[
\begin{align*}
\text{(3)} & \quad =\text{XOH} + H^+ \leftrightarrow =\text{XOH}_2^+ & \log K^{\text{int}}, \text{aluminol} &= -5.7 \\
\text{(4)} & \quad =\text{XOH} \leftrightarrow =\text{XO}^- + H^+ & \log K^{\text{int}}, \text{silanol} &= -6.25 \\
\text{(5)} & \quad =\text{XOH} + Na^+ \leftrightarrow =\text{XO}^-\text{-Na}^+ + H^+ & \log K^{\text{int}}, \text{silanol} &= -3.5 \\
\text{(6)} & \quad =\text{XOH} + Na^+ \leftrightarrow =\text{XO}^-\text{-Na}^+ + H^+ & \log K^{\text{int}}, \text{aluminol} &= -9.15
\end{align*}
\]
\[ \equiv \text{XOH} + \text{Cl}^- + \text{H}^+ \leftrightarrow \equiv \text{XOH}_2^+ - \text{Cl}^- \quad \text{log} \, K^\text{int}, \text{aluminol} = -4.7 \, \text{(optimized)} \quad (8) \]

The equations and parameters used are summarized in Table S2.

Molecular dynamics modelling (MD). For MD simulations, we used the LAMMPS package [62] to simulate slab quartz and kaolinite surfaces with a quinoline film in vacuum and water. The system was periodic in \( x \) and \( y \) directions (dimensions: \( 29.50 \times 25.54 \, \text{Å}^2 \) for quartz; \( 20.52 \times 26.67 \, \text{Å}^2 \) for kaolinite) and open in the \( z \) direction. We used pppm long range electrostatic with a 12 Å cut off, a leapfrog integrator, an Andersen thermostat and a step size of 1 fs. The interaction between atoms was described by force field parameters from Butenuth et al. [63] for quartz, from ClayFF [64] for kaolinite and from SPC/Fw [65] for water. The interaction between system components was generated by combining force field parameters according to the geometric mixing rules.
3. Results and Discussion

3.1. The samples

The specific surface area of the Berea sandstone powder, determined by N$_2$ gas adsorption at 77 K was 1.3 m$^2$/g and by water vapor at 293 K was 1.7 m$^2$/g. The difference results from the hydrophilic nature of the sample. Such differences have also been observed for goethite [66]. XRD of powdered Berea sandstone showed that quartz dominates (86.0%) and other phases are minor, such as kaolinite (5.0%), albite (3.4%), muscovite mica (3.7%) and orthoclase (1.9%) (Table S3). Clays (i.e. kaolinite), observed in the pores in SEM images (Figures S1), have significantly higher surface area than quartz. For example, kaolinite surface area ranges from 8 to 22 m$^2$/g [48, 67, 68] so even minor kaolinite would significantly increase quinoline adsorption. Initial elemental analysis of the fresh sandstone indicated carbon (0.19%), hydrogen (0.06%) and no nitrogen. Cation exchange capacity, determined with the SrCl$_2$ method, was 0.12 ± 0.07 meq 100 g$^{-1}$ at pH 6.1. Taking into account the clay content (5%), this correlates roughly with 0.015-0.018 meq g$^{-1}$ for kaolinite measured by Zachara et al. [69] using the $^{22}$Na/Na method. Thus, the clay particles, though only a very small weight fraction of the sandstone, are the most likely significant contributor to quinoline uptake.

3.2. The surfaces

Surface composition (Tables S4, S5) for the sandstone wafers and powdered material showed elements expected for clay and other aluminosilicate minerals. Aluminum is present in kaolinite, albite, muscovite and orthoclase; potassium, in muscovite and orthoclase and sodium, in albite. Carbon is present in organic matter inherent in the sample and as carbon contamination on the surfaces (adventitious carbon). Higher C on the wafers than on the powdered material is explained
by contamination during cutting. In C 1s high resolution spectra (Table S5), we observed appearance of additional carbon peaks at 287.4 and 288.8 eV for wafers, which we ascribed for C=O and O-C=O bonds. These peaks are typical only for wafers after cutting procedure and were not found in powdered sample. Significantly less Al was observed on the thin section, explained by loss of some clay during wafers preparation and by attenuation of Al photoelectrons by the increased carbon.

Nitrogen was higher on the quinoline exposed Berea powder after the 24 hour treatment with 20 mM Q in 0.05 M NaCl, than with 20 mM Q in 0.7 M NaCl (Table S6). N/Si was five times higher when the sandstone powder was treated in the low ionic strength solution, indicating that quinoline adsorbs better at low ionic strength. However, there was no significant difference in N/Si ratio when the quinoline treated sandstone wafers were rinsed with HIS or with LIS. From this we can suggest that results qualitatively indicate that quinoline desorption does not depend on solution salinity.

The results of ζ potential data for wafers of Berea sandstone, quartz (100), alumina (0001) wafers and γ-alumina powder are summarized in Figure S2a-c. The isoelectric point (IEP) for the untreated sandstone and quartz (100) wafers were at a pH<2. For untreated alumina powder, initial IEP was 9.0 and for alumina (0001), 4.5, which is explained by differences in alumina surface coordination on the two types of samples [70, 71]. Thus, for untreated sandstone, ζ potential resembled that for clean quartz more than for clean alumina, which is expected because sandstone is dominated by quartz. After exposure to quinoline the IEP for the Berea wafer shifted from pH 2 to 4.0 and for quartz, to pH 4.5 for samples in HIS and to pH 4.0 for treatment in LIS. For the alumina wafer, the IEP shifted from pH 4.5 to 3.3 for HIS and 3.7 for LIS. An even larger shift in IEP, from 9 to 4, was observed for the γ-alumina powder in both solutions. These IEP shifts
demonstrate quinoline adsorption on all investigated surfaces. Because quinoline is a hydrophobic, ionizable compound, adsorption converts hydrophilic surfaces to hydrophobic. Generally, IEP for hydrophobic surfaces lies between 3 and 4 [72]. This is explained by preferential adsorption of OH⁻, equivalent to enhanced autolysis of interfacial water. This ionization is characterized by pK_w 6–8 [72, 73] meaning that for quartz and sandstone on one hand, and for alumina on the other, the IEP would shift in opposite directions after quinoline adsorption, to approximately the same value, between 3 and 4, as we observed (Figures S2a-c).

3.3. Quinoline adsorption and surface species modelling

For the adsorption experiments, we did not use the solutions that mimic seawater but instead, used solutions at two ion strengths (0.7 M and 0.05 M) made only with NaCl as the background electrolyte. Equilibration between solid and solution resulted in a pH shift during the experiments, but this was accounted for. The isotherms (Figure 1), which showed maximum adsorption near pH 6, were well fit by the Freundlich equation:

\[ \Gamma = K_F \cdot C^{1/n}, \]  

where \( \Gamma \) represents the amount of quinoline adsorbed; \( C \), the quinoline equilibrium concentration in solution; \( K_F \) and \( n \) are constants depending on temperature; \( \Gamma_{\text{max}} \), the maximum amount of adsorbed quinoline; and \( K \), the Langmuir equilibrium constant. The fitting results with these two equations are presented in Table S7.
The extent of quinoline adsorption is significantly higher in the 0.05 M NaCl solution, than at 0.7 M. Assuming the cross sectional area of a quinoline molecule [28] to be 27 Å² and close packing, we estimate the quinoline surface coverage for a monolayer would contain 6.1 µmole/m². With this coverage, the data from the Freundlich isotherm suggest that at least 1.3 layers of quinoline are adsorbed in 0.7 M NaCl, and 2 layers at 0.05 M. Fitting with the Langmuir equation (Table S7) suggests maximum coverage of 10 molecular quinoline layers at 0.05 M NaCl and 6 layers at 0.7 M NaCl.

**Figure 1.** Quinoline adsorption isotherms for sandstone powder at room temperature from solutions with ionic strength a) 0.7 M and b) 0.05 M, fit with the Freundlich isotherm. The data for pH 8.7 at high ionic strength could not be fit with the Freundlich equation.

The concentration of silanol and aluminol sites was determined from the mole fraction of minerals in the sandstone, specific surface area, suspended concentration and site densities. For capacitance, we used 2.4 F m⁻² for inner sphere and 0.2 F m⁻² for outer sphere adsorption [56]. Berea sandstone contains kaolinite and minor muscovite, a mica mineral with high surface area. For modelling, we considered kaolinite and muscovite together as “kaolinite” because the specific surface area, site density and surface acidity are similar [74]. Quartz contributed 86% and the
kaolinite+mica fraction, 9%. Using the measured surface areas for kaolinite (9.8 m$^2$/g) [75], Berea sandstone (1.7 m$^2$/g) and the calculated surface area for quartz (1.0 m$^2$/g), the surface site density for quartz [57] as 8 sites/nm$^2$ and for kaolinite [56], 6 sites/nm$^2$, we estimated the silanol site concentration, from quartz and kaolinite, to be 0.0045 mol/L and for alu

minol, from kaolinite, 0.002 mol/L. No attempt was made to vary any of the surface parameters, except the Cl$^-$ complexation constant. In the model, quinoline was allowed to interact with both $\equiv$SiOH and $\equiv$AlOH sites, forming inner and outersphere complexes. We also considered multilayer adsorption by introducing inner and outersphere complexes with two quinoline molecules.

In principle, different complexes could be responsible for quinoline adsorption, depending on pH and ionic strength. To make meaningful fits, we made initial assumptions about which binding modes dominate. Two bonding mechanisms are typically important: innersphere coordination, where the adsorbed molecule interacts directly with the surface functional group, and outersphere complexation, where at least one water molecule bridges the quinoline to the surface. Both of these coordination modes can link two neutral species, two charged species or one charged and one neutral species. Because electrostatic interactions typically dominate outersphere complexation, we assume both species to be charged. Innersphere complexation, however, probably forms between two neutral species or two charged species, forming a hemisalt. Behavior during adsorption can indicate which mechanism dominates.

Quinoline adsorption being highest close to pH 6, and more pronounced for higher ionic strength (Figure 1), could be explained by the pK$_a$ of quinoline (pK$_Q$). The protonated form, quinolinium ($QH^+$), dominates at pH<4.93. At pH>4.93, quinoline outnumbers quinolinium so the neutral form dominates adsorption. Outersphere complexes, such as $\equiv$SO$^-$-$QH^+$, require negative surface sites, i.e. significant for silanol sites (pK$_{SiO^-}$ = 6.25), when $QH^+$ can outcompete Na$^+$. Formation of
innersphere, van der Waals complexes, resulting from attractive polarization forces of the aromatic ring [36], is another mechanism that can result in quinoline uptake.

To choose the best model for the $\text{H}^+\text{SiOH}\equiv\text{AlOH}Q\text{Na}^+\text{Cl}^-$ system, we systematically tested combinations of complexes with different stoichiometric composition. All experimental data for all quinoline concentration, pH and ionic strength were treated simultaneously. The best fit (Figure 2) included the following surface reactions:

\begin{align}
\equiv\text{SiOH} + Q &\leftrightarrow \equiv\text{SiOH}Q \tag{11} \\
\equiv\text{SiOH} + Q &\leftrightarrow \equiv\text{SiO}^\text{-}Q\text{H}^+ \tag{12} \\
\equiv\text{AlOH} + 2Q &\leftrightarrow \equiv\text{AlOH}Q_2 \tag{13}
\end{align}

All other combinations of conceivable (charged and uncharged) surface complexes gave a much poorer fit to the experimental data. The best fit for the equilibrium constants for Reactions 11 to 13 are:

\begin{align}
\log K_{11\text{int}} &= 2.30 \pm 0.01; \\
\log K_{12\text{int}} &= 3.23 \pm 0.01; \\
\log K_{13\text{int}} &= 3.69 \pm 0.01.
\end{align}

We noted that these constants may be reliable because of the reasons mentioned above, in the discussion of the electrokinetic data. The ionization constant for interfacial water at a hydrophobic surface can differ markedly from that of bulk water. This necessarily entails changes in thermodynamics of the other surface reactions. Moreover, the interfacial electrical model should differ somewhat from the conventional one, i.e. the TLM [73]. For the sake of consistency, we
kept a well established site binding approach here, because such complication of an already complex system would be unjustified.

Figure 2. Comparison of data from the experiments (dots) and the model fits (lines) for the amount of adsorbed quinoline at a) 0.7 M b) 0.05 M ionic strength as a function of pH. Quinoline total concentration is indicated in mM.

The ≡SiOHQ, which represents the hydrogen bonded species, and ≡SiO⁻·QH⁺, which represents the outersphere complex, have the same stoichiometry [29]. In the outersphere complex, the proton is located within the β-plane of the electric double layer. The existence of these two complexes has been confirmed by infrared spectroscopy [76] and sorption studies [77] and are present in the model developed by Zachara et al. [29] for quinoline adsorption on amorphous silica. The ≡SiOHQH⁺ complex, that they included, is absent in our model. All attempts to include this complex significantly degraded the fit to experimental data. Instead, we include aluminol quinoline complex, ≡AlOHQ₂, which represents multilayer adsorption.

Ainsworth et al. [35] studied quinoline sorption on Na-montmorillonite and observed a distinct break in the slope. We did not observe such a break, but we investigated a different range of the
isotherm. Nevertheless, by regressing the four parts of each isotherm separately and plotting the power coefficient, $1/n$, for all parts of the isotherms (Figure 1) as a function of quinoline concentration, $1/n$ clearly increases with concentration and exceeds 1 at high pH, whereas at low pH, the trend is opposite (Figure 3a). This correlates with the increasing role of $≡\text{AlOHQ}_2$ as pH increases. Figure 3a shows that $n$ tends to 1 as concentration decreases so the Freundlich isotherm converts simply to Henry’s law.

![Figure 3](image)

**Figure 3.** a) The power coefficient, $1/n$, for the separate parts of all isotherms (Figure 1) as a function of quinoline concentration. Filled symbols represent the 0.7 M NaCl solution and open symbols, 0.05 M NaCl; b) dependence of quinoline adsorbed amount and surface complexes concentration distribution on pH at 20 mM quinoline and 0.05 M ionic strength

We also used FITEQL to find the dominant adsorption complex as a function of pH (Figure 3b). At pH<4.93, the most abundant dissolved quinoline species is QH$^+$ and the outersphere complex, $≡\text{SiO}^-\cdot\text{QH}^+$, dominates adsorption at pH<4. This is corroborated by separating Reactions 11 to 13 from surface and solution ionization effects [29] (Equations 14 to 17):

$$
≡\text{SiOH} + Q ⇔ ≡\text{SiOHQ}
\log K = 2.3
$$

(14)
\[ \equiv\text{SiO}^- + \text{QH}^+ \leftrightarrow \equiv\text{SiO}^+\text{QH}^- \quad \log K = 4.55 \quad (15) \]

\[ \equiv\text{AlOH} + 2\text{Q} \leftrightarrow \equiv\text{AlOHQ}_2 \quad \log K = 1.39 \quad (16) \]

\[ \equiv\text{SiO}^- + \text{Na}^+ \leftrightarrow \equiv\text{SiO}^-\text{Na}^+ \quad \log K = 2.75 \quad (17) \]

At pH>4, the adsorbed \(\equiv\text{SiO}^-\text{QH}^+\) species decrease as [QH\(^+\)] gives way to [Q] in solution and adsorption becomes dominated by the neutral hydrogen bonded complex, \(\equiv\text{SiOHQ}\). Adsorption near pH 4 is more complicated because it is a balance between the two forms. At high quinoline loading and pH>5, the biquinoline complex, \(\equiv\text{AlOHQ}_2\), becomes increasingly important for adsorption. Thus, the \(\equiv\text{AlOHQ}_2\) complex appears at high quinoline concentration and high pH as a result of increased adsorption, through the mechanism of formation of the surface hemi-salts [78, 79]. Another explanation of increased quinoline adsorption at pH>5, where quinoline adsorbs as a neutral molecule, can be a hydrophobic interaction between quinoline molecules which begins to play a significant role. At high quinoline concentrations, quinoline molecules prefer to interact with each other, rather than with water molecules on the surface. This is also reflected in our model by formation of bi-quinoline surface complex, \(\equiv\text{AlOHQ}_2\) at pH>5.

3.4. Atomistic interactions

To supplement our understanding of quinoline adsorption on sandstone and its interaction, we simulated quartz and kaolinite slabs with 50 quinoline molecules in a molecular dynamics study. All surface groups and quinoline molecules were kept in their neutral form because the sorption experiments and FITEQL modelling indicated SiOHQ to be the dominant surface complex. The highest adsorption was over 5<pH<8, where quinoline is neutral and, though the mineral surface
in principle has a negative surface charge at pH>IEP, large fraction of ionizable sites remain protonated.

The first simulations were carried out in vacuum and resulted in a film of adsorbed quinoline molecules. The radial distribution function and single molecule surface coordination geometry are depicted in Figure 4a for quartz and Figure 4b for kaolinite. The dominant peak in Figure 4a at 2.95 Å represents the O–N interaction and shows that quinoline attaches to the surface predominantly through strong SiOH–N hydrogen bonding with weaker contributions from van der Waals interactions with carbon atoms. This upright quinoline coordination maximizes the number of hydrogen bonding quartz–quinoline interactions and promotes effective packing through π-stacked lateral interactions. Though the majority of quinoline molecules attached upright on quartz, molecules lying flat on the surface were also seen in the simulation. The first hydrogen bonded layer served as anchor points between the polar surface and additional quinoline molecules. The radial distribution function and quinoline molecule coordination mode were in many ways similar on kaolinite (Figure 4b). Molecules coordinated upright in a way that maximized hydrogen bonding to the surface and allowed lateral π-stacking. Some molecules attached through single hydrogen bonds (Figure 4a), whereas others attached through double hydrogen bonding (Figure 4b).
**Figure 4.** a) Adsorbed quinoline – quartz and b) adsorbed quinoline – kaolinite interaction. The radial distribution function depicts the interaction between neutral surface –O(H) groups with the quinoline nitrogen (blue) and carbon (gray) atoms in vacuum (dashed lines) and in solution (solid line). The dominant quinoline coordination is upright, maximizing quinoline–surface hydrogen bonding; H (white), C (cyan), N (blue), O (red), Al (pink) and Si (yellow).
The radial distribution functions depicted in Figures 4a and 4b are different from traditional RDFs for ions in liquids, which usually show short range correlation with first and (sometimes) second sphere ligand coordination. The periodicity of the surface and adsorbed molecule packing restricts quinoline movement and produces undulations in the RDF, which can be seen at 8-10 Å for the nitrogen RDF (Figure 4b). Because the quinoline molecule takes up more than one surface -O(H) site and the molecules have some variation in coordination and freedom to move, attachment is not traditional Langmuir adsorption even though it can effectively be treated as such, for all practical purposes.

From the MD simulations, we estimated how much quinoline adsorbs. By defining an adsorbed molecule as having at least one atom within 3.5 Å from the solid oxygen layer, we calculated an average of 22 molecules attached to quartz in vacuum and 23 molecules in water. This corresponds to 2.9 and 3.0 molecules per nm². For kaolinite, the densities were 16.9 molecules in vacuum and 16.0 in water, translating to 3.1 and 2.9 molecules per nm². The results correspond with quinoline packing in an upright, π-stacked position, which would take ~3.5×8.25 Å² (0.29 nm²) per molecule or 3.5 molecules/nm². This is the upper limit; adsorption controlled by surface atomic structure would decrease real density. Considering specific quinoline–surface interactions would decrease packing density because of mismatches between the two cells. Estimates for lying flat compared with upright coordination give 1.9 and 4.6 molecules per nm². The flat configuration would be stabilized by significant van der Waals interaction between the surface and quinoline molecules whereas the upright position cannot form any reasonable electrostatic interactions with the surface. Stability relies on π stacking between molecules. Nevertheless, our data show that upright coordination (Figure 4) dominates, meaning that quinoline molecules occupy 2 silanol and 2.7
aluminol surface sites because their density, 3 nm$^{-2}$, is lower than the 6 nm$^{-2}$ silanol and 8 nm$^{-2}$
aluminol site densities.

The change in power coefficient, $I/n$, as a function of quinoline concentration and pH (Figure
3a) also give insight into coordination. Low coordination at low pH and generally at low ionic
strength, suggests stronger adsorption as surface density increases. Such cooperative adsorption
reflects a) attractive interactions between adsorbed neighboring molecules or b) sorbate clustering
[80, 81]. Both imply significant lateral interaction, which is consistent with π-stacking between
neighboring quinoline molecules (Figure 5A). The reverse, where $I/n>1$ and its increase with
concentration for some of the high pH data, imply that quinoline molecules are held more weakly
as adsorption increases. Such anticooperative adsorption can reflect a) quinoline–quinoline
repulsion at high surface loading, b) binding to progressively less favorable sites with increased
load or c) chemisorption as a significant component of the binding mechanism. At pH between the
IEP and the quinoline pK$_a$, surface sites are predominantly deprotonated and quinoline molecules
are protonated suggesting that $\equiv$SiO$^-$-QH$^+$ is the dominant adsorption mechanism. This outersphere
adsorption, or potentially hemisalt formation, is cooperative, whereas in the higher pH range,
where neutral quinoline molecules bind to charged surface sites, adsorption is anticooperative.
When a quinolinium cation adsorbs to a vacant site next to an occupied site, as in hemisalt
adsorption, it introduces an additional repulsive Coulombic interaction with the neighboring
quinolinium ion, as depicted in Figure 5, pane B.

Quinoline adsorption from the low ionic strength solution probably results from lower surface
charge. In general, an ionizable surface has fewer charged sites in low salinity than in high.
Because quinoline predominantly binds to quartz and kaolinite surfaces as a neutral molecule,
there are more surface sites for it to bind to in low salinity water. That quinoline remains adsorbed, suggests a large kinetic barrier for desorption.

\[ \text{Figure 5. Lateral interactions between quinoline molecules. Significant quinoline } \pi \text{-stacking gives rise to strong cooperative binding to sandstone at pH 3.9, where quinoline forms an outersphere or hemisalt complex with the surface (A), whereas the overall adsorption is anticooperative for quinoline binding at higher pH, where quinoline forms a neutral surface complex (B).} \]

4. Conclusions

Our results suggest that NHCs would tend to be mobile in groundwaters with high salt concentration, such as oil spills in sediments where the pore water approaches seawater salinity or directly under municipal waste storage sites, but that further afield, if the ionic strength dropped, NHCs would adsorb, mostly to clay, in the normal groundwater pH range, and remain there. XPS surface investigations qualitatively demonstrated that decreasing the salinity of water used to wash out NHCs from contaminated soil and aquifers potentially would have little positive effect. Further investigation of quinoline adsorption to surface hydroxyl groups will help in designing water
treatment strategies using artificial materials, such as stone wool fibers or other materials which inherently contain aluminol and silanol surface sites.

Supporting Information

Additional data includes SEM-EDXS images of Berea sandstone polished thin section, zeta potential data and tables with solution compositions, FITEQL modelling parameters, XRD, XPS and adsorption isotherm fitting results.

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