

INTERNATIONAL CONFERENCE ON OIL SHALE AND SHALE OIL

May 16-19, 1988 Beijing, China

A Mechanistic Study of Sorption of Quinoline and Pyridine onto Rundle Spent Shale

S. Zhu, P.R.F. Bell and P.F. Greenfield
Department of Chemical Engineering
University of Queensland,
St Lucia 4067, Australia

ABSTRACT

The sorption of pyridine and quinoline from dilute aqueous mixtures onto Rundle spent oil shale over a wide pH range has been investigated. Single solute adsorption-desorption isotherm and bisolute adsorption isotherm studies were conducted at the natural pH of the mixtures. The results show that the specific adsorption of both pyridine and quinoline is highly dependent on pH and that a maximum adsorption occurs for both at around pH4. A maximum occurring at this pH indicates that the cationic species of the organics dominates the sorption process at lower pH. The sorption of pyridine seems to be dominated by simple cation exchange while that of quinoline appear more complicated - chemisorption of quinolinium is included. At high pH adsorption of the molecular species occurs. Coordination with the exchangeable cations appears to be an important factor for pyridine adsorption while surface protection and/or chemisorption appears important for quinoline. Sorption isotherms for both single component and the bisolute mixtures at the natural pH of 8 are of the L-4 type. At low concentrations the isotherms are reversible. Little competition is evident from the bisolute adsorption studies which indicates that multicomponent adsorption in such systems is predictable from the single solute isotherms.

1. INTRODUCTION

Previous studies [1][2] have shown that spent shale could prove to be a useful adsorbent for the removal of organics and in particular the N-heterocycles, from retort water.

The Rundle spent shale used in the present study was extracted from the Kerosene Creek seam, Rundle deposit, Queensland and processed in the Lurgi pilot retort in Frankfurt in 1980. The spent shale consists mainly of quartz with a small amount of clays (e.g. montmorillonite, illite and kaolinite), various metal oxides and salts. While no detailed work has been reported on the adsorption of N-heterocyclic compounds onto spent shale, there are reports of such adsorption onto other natural supports. Baker and Luh [3] [4] studied pyridine adsorption by clays in aqueous solutions. Their results showed that

significant adsorption only occurred from acidic solutions, with maximum adsorption occurring at about pH4. These results implied cation exchange as the principal adsorption mechanism. Other studies [5] show evidence of the adsorption of the pyridine molecule by clays. In these studies coordination of the pyridine molecule to the adsorbed exchangeable cations was implicated as the mechanism of adsorption.

Helmy et al [6] investigated quinoline adsorption from aqueous solutions by clays and clay-like materials and found that the adsorption isotherms have two plateaux, each of the isotherms resemble a Langmuir curve. They also found that adsorption was a strong function of pH with a maximum occurring at pH6. These results also implied cation exchange as the mechanism of adsorption in the lower pH range. It is noted that adsorption of molecular quinoline was accompanied by an average increase of 0.3 pH units, indicating that hydrolysis of adsorbent cations and/or chemisorption of quinoline takes place.

It is known that the particular Rundle spent shale used in this work does exhibit a significant cation exchange capacity (~ 20 mg/100g) [7] and hence should behave in a manner similar to the clay-like materials used in the above studies.

2. MATERIALS AND METHODS

The chemical composition of the Rundle spent shale and cation exchange properties are given in detail elsewhere [7]. XRD analysis shows this material to consist of mainly quartz with small amounts of non-expanding smectites and expanding montmorillonite. Analytical grade chemicals were used in all experiments.

Previous studies [11] have noted that significant microbiological degradation of pyridine-water mixtures can occur during batch adsorption tests. No reports were found of quinoline degradation. Zhu et al [13] studied the stability of pyridine and quinoline in aqueous solutions, some of which were contacted with spent shale. Both pyridine and quinoline were shown to degrade ultimately after contacting with spent shale, but no significant changes were observed within the first two days. For solutions which were not contacted with spent shale, neither pyridine nor quinoline showed any degradation over the observed test period of two weeks.

The pH adjustments were made by the addition of NaOH or HCL (0.1N) before the addition of quinoline or pyridine. The reported pH values are the equilibrium values after adsorption. For adsorption tests a 5g portion of air-dried spent shale was placed in a 150 ml conical flask and 50 ml of solution was added which contained known pyridine and/or quinoline concentrations. The flasks were sealed with rubber-stoppers and then placed in an orbital shaker water bath. The tests were carried out for a 24 hour period at 150-160 rpm and 25°C. After 24 hours the flasks were centrifuged at 1000 rpm for about 20 minutes in order to obtain the supernatant solutions. A 20 ml solution sample was withdrawn from each flask for analysis. The pyridine and quinoline concentrations

in the single component systems were measured by a U.V. spectrophotometer at wavelengths of $254\ \mu\text{m}$ and $312\ \mu\text{m}$ respectively. For the bisolute system, the concentration was measured using HPLC with a U.V. detector set at the above wavelengths. The amount of solute adsorbed per unit mass of solids was calculated based on a mass balance.

Desorption tests were also carried out. After 20 ml of adsorbed supernatant was withdrawn as mentioned above, 20 ml of distilled water was added into each of the flasks. The flasks were then stoppered, shaken and centrifuged using the same procedure as that used during the adsorption tests. 20 ml of supernatant was withdrawn from each of the flasks and analysed. Following the adsorption tests, some solids were separated from the flasks by successively mixing and decanting the suspended fines from the solid-solution mixture. These fines were analysed by XRD to determine the basal spacings of montmorillonite in the spent shale.

3. RESULTS AND DISCUSSION

Effects of PH on Adsorption

Figures 1 and 2 summarise the adsorption results as a function of pH. It is noted that both curves pass through a maximum at pH4.

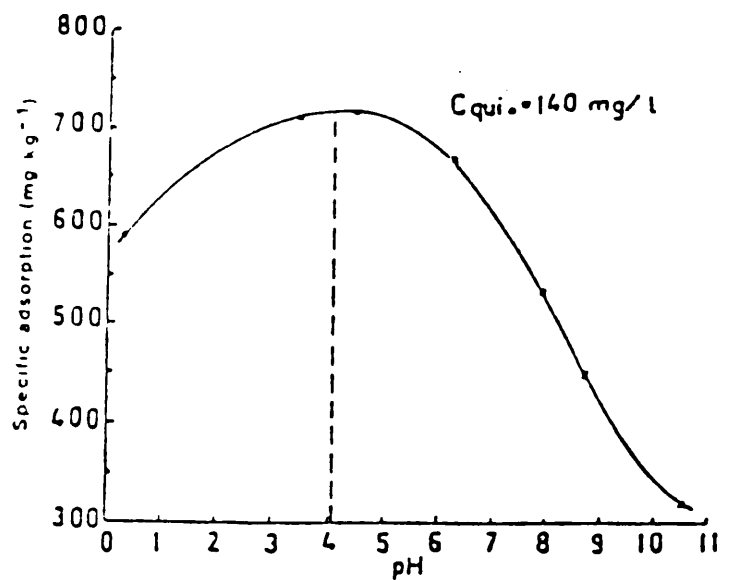
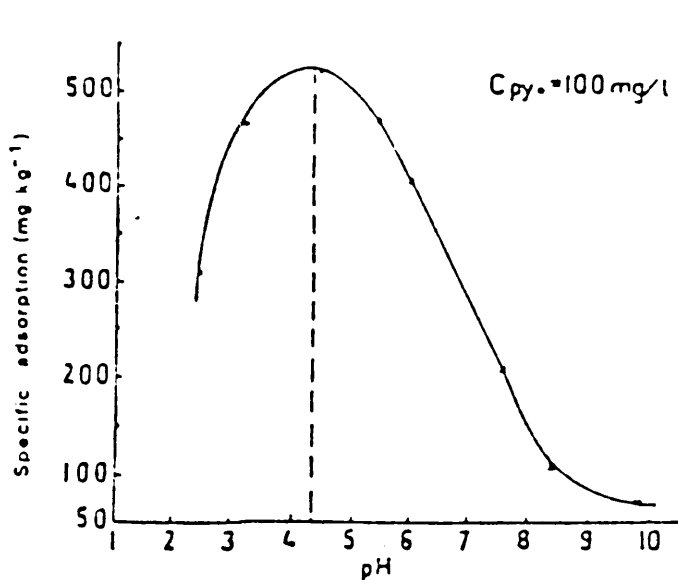
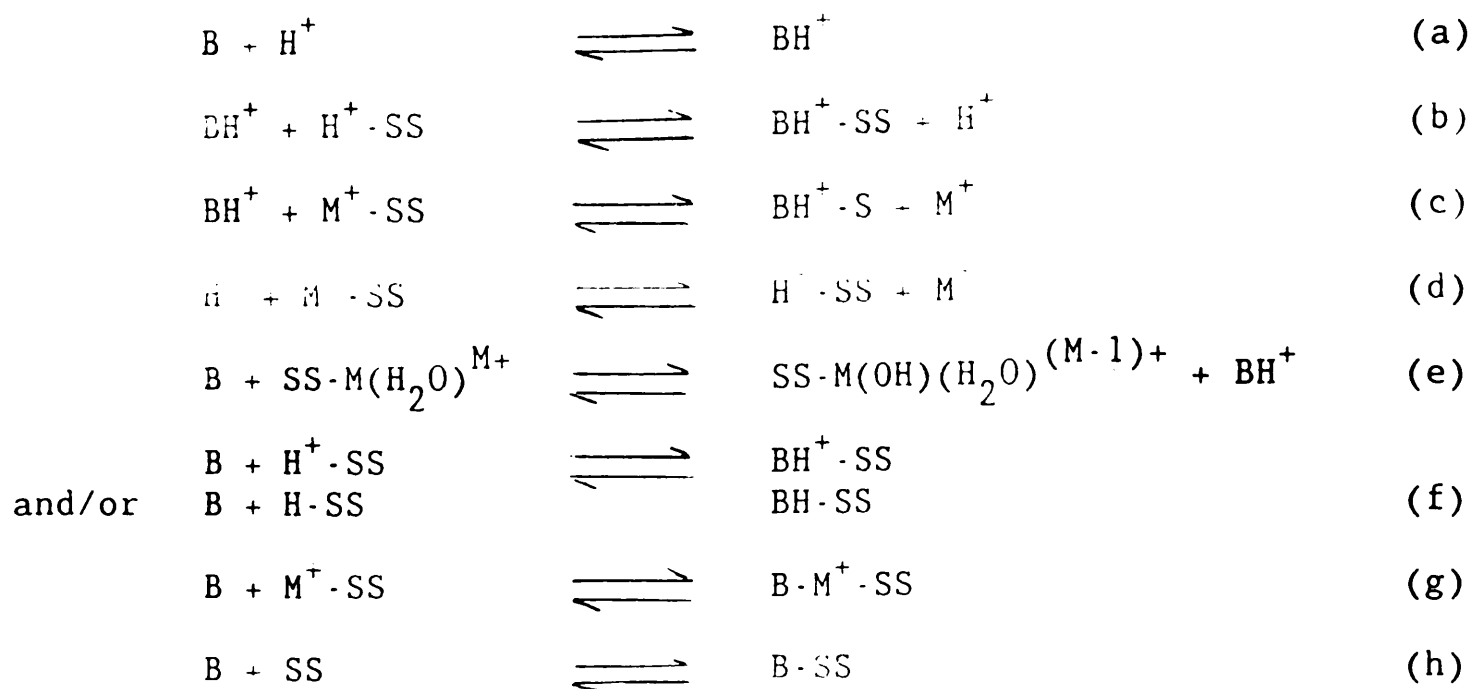


Fig. 1 Effect of PH on Pyridine adsorption

Fig. 2 Effect of Ph on Quinoline adsorption

The observed shapes of these curves result from a number of chemical interactions between the various ionic species (organic and inorganic), the organic molecule species and the spent shale surface. Usually, as pH increasing the surface negative charge increases and the ratio of organic cation to organic molecule decreases.

The interaction of pyridine and quinoline with the spent shale surface can be summarised as follows [8] [9] [15]

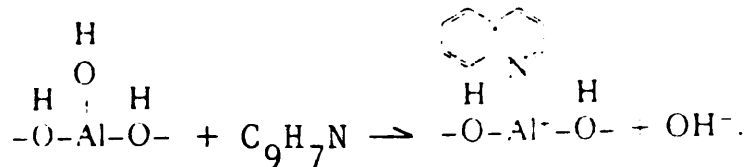


Where M^+ represents the exchangeable metal cations on the spent shale surface (SS) while H^+ refers to hydronium in H_3O^+ . At $\text{pH} < \text{pKa}$ ((pKa)_{py} = 5.2; (pKa)_q = 4.9)[10] equations (a) to (d) will dominate and at $\text{pH} > \text{pKa}$ equations (e) to (h) will dominate.

The observed maxima in Figs. 1 and 2 result from the competing of molecular versus ionic species besides the change of surface charge. The peaks for both curves are about 1 pH unit below the respective pKa. This demonstrates that the ionic of the respective organic molecules dominate the adsorption process. The rapid drop-off of the pyridine adsorption at $\text{pH} < 4$ is attributed to displacement of the pyridinium by the hydronium through a simple cation exchange process (see equation (b)). It is interesting to note that such a rapid drop-off does not occur so much for quinoline. This indicates that the quinolinium has a much higher selectivity than that of pyridinium to hydronium and/or more likely that specific reactions (e.g. chemisorption) between the quinolinium ions and the surface of spent shale occur.

At $\text{pH} > \text{pKa}$ equations (e) to (h) will become most important. Detailed studies [11] have indicated that molecular pyridine coordinates to the exchangeable metal cations (see equation (g)). In other studies [6][10] coordination is not indicated in the adsorption of quinaline molecules. It is suggested that surface protection [10] and chemisorption reactions [6] might be more important for quinoline.

It is noted that the specific adsorption of pyridine drops off rapidly with increasing pH while the specific adsorption of quinoline is maintained at a much higher level. The less rapid drop-off for the quinoline supports the concept of surface protonation and a chemisorption. In the later case it is suggested that quinoline replace surface hydroxyls bonded to structural atoms, such as Al and Fe [6]:



Physical adsorption by Van der Waals force may also occur as equation (h).

Single Component Isotherms

Figures 3 and 4 show the single component sorption isotherms for quinoline and pyridine in aqueous spent shale mixtures. The pH of all these mixtures was constant at 8. At this high pH one can assume that the organics in solution are present in the molecular species only.

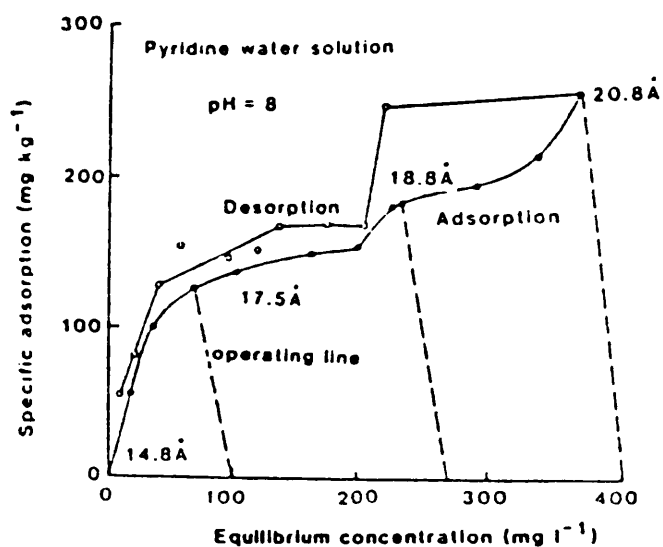


Fig. 3 Adsorption and desorption isotherms for Pyridine.

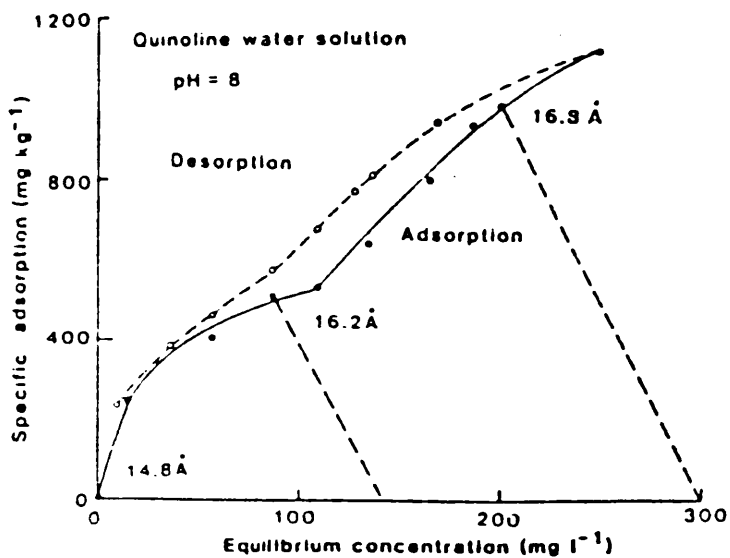


Fig. 4 Adsorption and desorption isotherms for Quinoline.

The single component isotherms are of L-4 type with two plateaux according to classification by Giles et al [14]. The first plateau is often attributed to the completion of a monolayer coverage and the second to either a second layer or reorientation of the adsorbate molecules, thus obtaining a denser packing. XRD analysis (Figs. 3,4) supports the latter explanation in that there is a general increase of the basal spacing with increased uptake of adsorbate. The desorption isotherms in Figures 3 and 4 show that up to the first plateau the adsorption is essentially reversible, while at higher concentrations irreversible.

Bi-Solute Isotherms

The results from the sorption studies with the bisolute mixtures are presented in Figures 5 and 6. These results demonstrate that in the lower concentration range little competition exists between the two solutes.

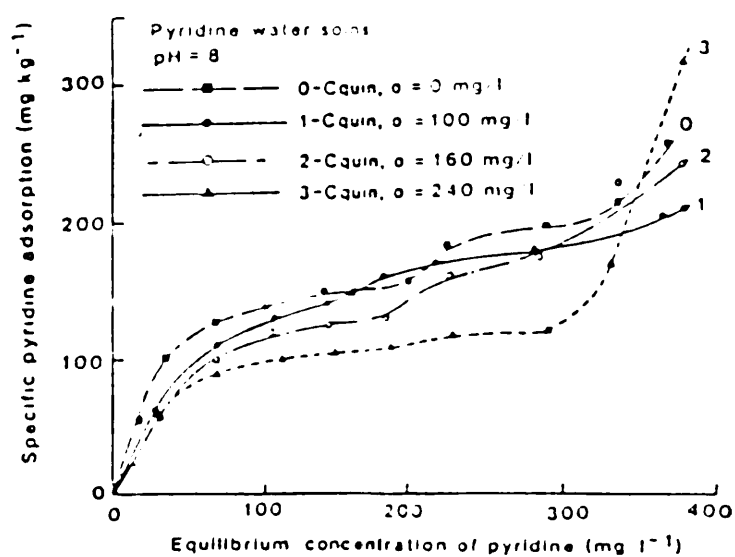


Fig. 5 Adsorption isotherms for Pyridine in presence of Quinoline

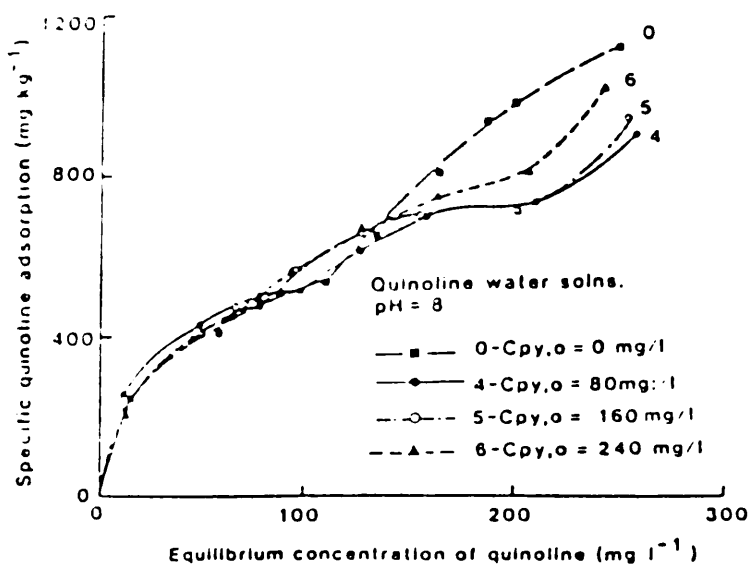


Fig. 6 Adsorption isotherms for Quinoline in presence of Pyridine

The result is significant in that at the usual concentrations of pyridine (20-80 mg/l) and of quinoline (20-50 mg/l) in retort water no significant competition should be observed. In such cases, therefore, the single adsorption isotherm should predict the adsorption for each component in the multicomponent system.

4. CONCLUSIONS

The specific adsorption of both quinoline and pyridine depends strongly on the pH of solution. A maximum adsorption for both of these N-heterocyclic compounds occurs at about pH4 indicating that the ionic species are dominant in the adsorption process at low pH.

At high pH other factors (e.g. coordination, surface protrusion, solvent interaction) which affect the adsorption of the molecular species become important. The results indicate that chemisorption of quinoline may also be important at high pH.

The adsorption isotherms for low concentrations of the solutes at the natural mixture pH of 8 for both pyridine and quinoline are well represented by the Langmuir model. No significant competition was observed in the low concentration bisolute adsorption studies. Thus, the Langmuir monolayer equations can be used to predict the bisolute adsorption in relatively low concentrations (less than 100-150 mg/l).

These results are highly significant when one considers the adsorption of a complex mixture such as retort water onto spent shale. The results of pyridine and quinoline indicate that this adsorption is reversible. The implication of these findings for the co-disposal option are that spent shale is a relatively good adsorbent for the basic fraction of impurities in retort water, however, if subsequent leaching of the spent shale occurs there will be release of the basic compounds back into solution if subsequent degradation of the basic organics has not already occurred.

REFERENCES

1. J.P. Fox et al., 13th Oil Shale Symp. Proc., Colorado School of Mines, Golden, Colorado, 321(1980)
2. P.R.F. Bell et al. Proc. of the 2nd Aust. Workshop on Oil Shale, Brisbane 282(1984)
3. R.A. Baker & M.D. Luh. Wat. Res. 5.839 (1971)
4. M.D. Luh & R.A. Baker. Wat. Res. 5.849 (1971)
5. B.K.G. Theng. "The Chemistry of Clay-organic Reactions". Adam, Hilger, London, 110 (1974)
6. A.K. Helmy et al., Clay Clay Min., 31, 29 (1983)
7. A.A. Krol et al., Wat. Res. 20.1299 (1986)
8. J.B. Weber, Amer. Mineralogist, 51, 1657 (1966)
9. G. Sposito, Chapter 2 in: The Surface Chemistry of Soil (Oxford Univ. Press, New York, 1984)
10. J.M. Zachara, Environ. Sci. Tech. 21, 4, 397 (1987)
11. S. Zhu et al, Proc. of the 4th aust. Workshop on Oil Shale 138 (1987)
12. S. Zhu et al 1987b (unpublished)
13. S. Zhu et al 1986 (in preparation)
14. C.H. Giles et al., J. Colloid and Interface Science 47,3,755 (1974)
15. V.C. Farmer and M.M. Montland. J. Chem.Soc. (A) 344 (1966)