2265

## HIGHLY SELECTIVE PENETRATION OF RED INK IN A SALINE WATER

#### by

## Chan-Juan ZHOU, Dan TIAN, and Ji-Huan HE<sup>\*</sup>

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou, China

> Original scientific paper https://doi.org/10.2298/TSCI1904265Z

Water pollution has become a major global problem and requires an immediate action. It was generally considered that pollutants were diffused gradually from surface to underwater region, where plants and animals should have less affected. However, diffusion of contamination is very slow in comparison with penetration. Here we show saline water has a highly selective penetration, and the penetration rate is much higher than that of diffusion. An experiment was carried out using a drop of red ink as a point pollution source to check both diffusion and penetration processes in various salt solutions with different concentrations, the salt concentration greatly affects the penetration process and there is a threshold value beyond which no penetration occurs. An imaged capillary is adopted in this paper to explain the selective penetration on a molecular scale, revealing that the salt concentration and temperature will greatly affect the capillary pressure and the penetration depth. Our results demonstrate that the penetration is the main pollution dispersion, and we anticipate our theory would shed light upon the major pollution problem from theoretical analysis to pollution control.

Key words: underwater pollution, capillary pressure, selective penetration, selective adsorption, lattice, nano/micro scale porous medium, selective oxidation

## Introduction

Water pollution has become a major environmental problem and a serious social problem as well. In some developing countries, the problem has become ever worse. It is the very time to control water pollution and pollution dispersion. It was generally considered that the diffusion was main dispersion of pollutants. According to the Fick's law, a pollution source with high pollutant concentration will diffuse to a region of low concentration, and the diffusion ratio depends upon the concentration gradient. However, some counter-examples were reported in open literature, Fiume and Mattioli [1] injected intravenously the L-[3H]SA-ara-AMP conjugates to mice to check the diffusion process, and the results demonstrated that the diffusion did not follow Fick's law, the vast majority was dispersed to the liver, only small quantities were taken up by brain, spleen, bone marrow and intestine. This phenomenon is called the selective penetration.

Selective penetration has been observed in various fields, Sun *et al.* [2] found the selective ion penetration of sodium salts through a graphene oxide (GO) membranes, while heavy-metal salts infiltrated much more slowly, especially copper salts were entirely blocked

<sup>\*</sup> Corresponding author, e-mail: hejihuan@suda.edu.cn

by GO membranes. Richards and Weygandt [3] found that fat solvents can selectively penetrate into the nervous system of mosquito larvae. Dai, *et al.* [4] revealed selective penetration of metal atoms. Hoefner, *et al.* [5] used polymer gels to improve waterflood performance in petroleum engineering, and they found that selective gels flow preferentially into higherpermeability media and resist penetration into tighter media. Zarlenco and Abrams [6] gave evidence for the selective penetration of free base into streptococcus fecalis cells. However, the mechanism of the selective penetration is not clear yet, this paper gives an experimental study on selective penetration and give an explanation using capillary action.

## Experiment

In our experiment, a bottle of red ink was bought in a market near Soochow University, which was used for penetration experiment in various solutions. The 7.4% Na<sub>2</sub>CO<sub>3</sub> solution and 7.4% NaCl solution were prepared, and a transfer liquid gun was used to move a drop of red ink onto the surfaces of the prepared solutions to see the penetration phenomenon.

Figure 1 shows that the red ink in the  $Na_2CO_3$  solution dropped immediately into the bottom of the bottle due to gravity, neither diffusion nor penetration phenomenon was observed during the dropping process. The red ink then went up gradually and finally distributed on the solution surface. After 20 minutes, the whole solution became brown. For NaCl solution, a quite different phenomenon was observed, see fig. 2. The red ink began to penetrate into the solution as soon as it encountered the solution surface, no jet of the red ink was found as that for the Na<sub>2</sub>CO<sub>3</sub> solution. During the penetration process, the red ink also diffused in radial direction. After 20 minutes, the whole solution became soft red.

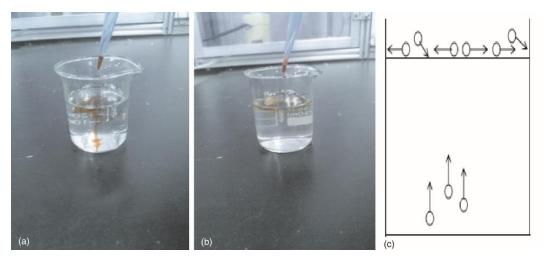


Figure 1. No penetration of red ink for Na<sub>2</sub>CO<sub>3</sub> solution; (a) a red ink jet was observed due to gravity, (b) the jet went up to the surface and diffused on the surface, (c) the diffusion model

In order to study the effect of salt concentration on the penetration process, we prepared for NaCl solutions with concentrations of 0% (pure water), 5%, 10%, 15%, 20%, and saturated salt water, respectively. A drop of red ink was moved onto the surface the above solutions simultaneously. The pure water sees diffusion at the bottom of the bottle when the red ink jet reached the bottom, while the saturated salt water can see the rebound of the red ink jet from the bottom rapidly and a clear separation layer can be observed on the solution surface at

#### 2266

the initial stage, see fig. 3(a). It is obvious that there is a threshold value for the concentration beyond which no penetration process happens, and dropping red ink will be rebounded at a higher velocity for a higher salt concentration. Only NaCl solution with concentration of 5% has the obvious selective penetration, NaCl solutions with concentration of higher than 10% block penetration, and only diffusion is happened. After 40 minutes, all solutions became homogeneous and the same color was observed, see fig. 3(c).

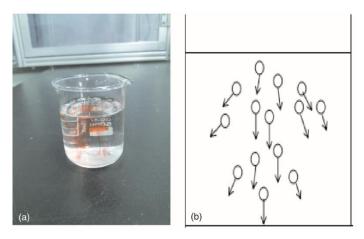


Figure 2. Selective penetration of red ink into NaCl solution; (a) a red ink was penetrated into the solution with diffusion, (b) the penetration model

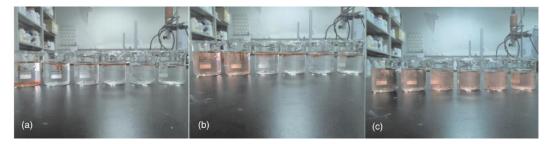


Figure 3. Selective penetration of red into into NaCl solutions with different concentrations of 0% (the left-most bottle), 5%, 10%, 15%, 20%, and saturated salt water (the right-most bottle), respectively; (a) initial stage, (b) after 10 minutes, (c) after 40 minutes

# Theoretical explanation of the selective penetration

Though the selective penetration has been reported in various fields, and it has wide applications in tissue engineering for rapid penetration of the released drug into a tissue regeneration (e. g. bone restoration), and capillary refining on the iron and steelmaking processes [7], imbibition of fluid in porous medium, its mechanism is still unclear.

In this paper we will explain selective penetration using capillary theory. A solution on molecular scale can be considered as a discontinuous lattice. Figure 4 is the water lattice, we can draw a zig-zag curve linking the adjacent points as illustrated in fig. 4, and an imagined zig-zag tube is formed, and we call it an imagined capillary.

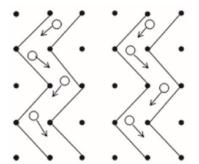


Figure 4. An imagined capillary revealing the penetration process

The capillary height, h, can be derived by Young-Laplace equation:

$$h = \frac{2\sigma\cos\theta}{\lambda\rho \mathrm{g}r} \tag{1}$$

where  $\sigma$  is the liquid-air surface tension, g – the gravity acceleration, r – the equivalent radius of the imaged capillary tube,  $\theta$  – the contact angle,  $\rho$  – the density of the solution, and  $\lambda$  – the correction factor of the zig-zag shape.

We modify eq. (1) in a more practical way:

$$H \propto \frac{1}{\rho L} \tag{2}$$

where H is the penetration depth and L – the distance between two adjacent points of the water lattice, or the average space distance between molecules.

The solution density and lattice space strongly depend upon concentration and temperature:

$$L = L(C,T) \tag{3}$$

$$\rho = \rho(C, T) \tag{4}$$

where C is the concentration and T – the temperature.

It can easily find the relationship of eq. (4) experimentally, a higher temperature results in lower density of salt water, and a higher concentration leads to a higher density.

A high temperature will relax molecular forces (*e. g.* ionic bonds and Van der Waals force), as a result, the lattice space is enlarged. The increase of salinity will destroy the lattice structure of water molecules, and the equivalent the lattice space increases accordingly. For a constant temperature, the lattice space and density of the salt water can be expressed in a power series:

$$L = a_0 + a_1 C + a_2 C^2 + \dots + a_n C^n$$
(5)

$$\rho = b_0 + b_1 C + b_2 C^2 + \dots + b_m C^m \tag{6}$$

and the penetration depth can be written in the form:

$$H = \frac{H_0}{(b_0 + b_1C + b_2C^2 + \dots + b_mC^m)(a_0 + a_1C + a_2C^2 + \dots + a_nC^n)}$$
(7)

where  $a_i(i=1 \sim n)$ ,  $b_i(i=1 \sim m)$ ,  $H_0$  are constants which can be determined experimentally.

Equation (7) implies that a higher concentration always results in a lower capillary pressure or a shorter penetration depth.

### Conclusions

It was considered that mesopelagic ecosystem will be less affected by the surface pollution, but the selective penetration process of some pollutants will greatly damage not only epipelagic and mesopelagic community, but also bathypelagic and below creature. The selective penetration sheds a light on insight into the pollution mechanism at underwater/undersea zones and a possible control of water pollution.

Selective adsorption [8-12] and selective oxidation [13-15], in nano/micro scale porous media can be explained alternatively by selective penetration. For example, a leaf constitutes of cell lattice, and an imagined capillary can produce capillary pressure to selectively absorb gas or nanoparticles, as a result, selective oxidation or selective adsorption can be observed. This results are helpful to design a nanofiber membrane by either electrospinning or bubble electrospinning or macromolecular electrospinning [16-23].

## Acknowledgment

The work is supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), National Natural Science Foundation of China under grant No. 11372205.

#### References

- Fiume, L., Mattioli, A., *et al.*, Selective Penetration and Pharmacological Activity of Lactosaminated Albumin Conjugates of Adenine Arabinoside 5-Monophosphate (ara-AMP) in Mouse Liver, *Gut*, 25 (1984), 12, pp. 1392-1398
- [2] Sun, P., et al., Selective Ion Penetration of Graphene Oxide Membranes, ACS Nano, 7 (2013), 1, pp. 428-437
- [3] Richards, A. G., Weygandt, J. L., The Selective Penetration of Fat Solvents into the Nervous System of Mosquito Larvae, *Journal of the New York Entomological Society*, 53 (1945), 2, pp. 153-165
- [4] Dai, J., et al., Selective Penetration of Metal Atoms New Evidence and Application for the Simple Ideal Penetration Model of the Long-Chain Close-Packed Alkanethiol Self-Assembled Monolayers on Au(111), Physics Procedia, 32, (2012), Dec., pp. 198-205
- [5] Hoefner, M. L., et al., Selective Penetration of Biopolymer Profile-Control Gels: Experiment and Model, Journal of Petroleum Science and Engineering, 7 (1992), 1-2, pp. 53-66
- [6] Zarlenco, M., Abrams, A., Selective Penetration Of Ammonia And Alkylamines Into Streptococcus Fecalis And Their Effect Of Glycolysis, *Biochimica et Biophysica Acta*, 71 (1963), 1, pp. 65-77
- [7] Tanaka, T., et al., Trial on the Application of Capillary Phenomenon of Solid CaO to Desulfurization of Liquid Fe, ISIJ International, 50 (2010), 8, pp. 1071-1077
- [8] Kong, H. Y., et al., Highly Selective Adsorption of Plants' Leaves on Nanoparticles, Journal of Nano Research, 22 (2013), May, pp. 71-84
- [9] Lorzing, G. R., et al., Selective Gas Adsorption in Highly Porous Chromium(II)-Based Metal-Organic Polyhedra, Chemistry of Materials, 29 (2017), 20, pp. 8583-8587
- [10] Xu, G., et al., Highly Selective and Efficient Adsorption of Hg<sup>2+</sup> by a Recyclable Aminophosphonic Acid Functionalized Polyacrylonitrile Fiber, Journal of Hazardous Materials, 344 (2018), Feb., pp. 679-688
- [11] Yuan, D., et al., Highly Selective Adsorption of Uranium in Strong HNO<sub>3</sub> Media Achieved on a Phosphonic Acid Functionalized Nanoporous Polymer, *Journal of Materials Chemistry*, 5 (2017), 43, pp. 22735-22742
- [12] Yoon, J. W., et al., Highly Selective Adsorption of CO over CO<sub>2</sub> in a Cu(I)-Chelated Porous Organic Polymer, Journal of Hazardous Materials, 341 (2018), Jan., pp. 321-327
- [13] Faraji, A. R., et al., Synthesis and Characterization of Cobalt-Supported Catalysts on Modified Magnetic Nanoparticle: Green and Highly Efficient Heterogeneous Nanocatalyst for Selective Oxidation of Ethylbenzene, Cyclohexene and Oximes with Molecular Oxygen, Journal of Colloid and Interface Science, 506 (2017), Nov., pp. 10-26
- [14] Xu, Q., et al., Two New Sandwich-Type Polyoxomolybdates Functionalized with Diphosphonates: Efficient and Selective Oxidation of Sulfides to Sulfones, *Materials*, 10 (2017), 10, pp. 1173
- [15] Liu, P., He, J. H., Geometric Potential: an Explanation of Nanofiber's Wettability, *Thermal Science*, 22 (2018), 1, pp. 33-38

- [16] Peng, N. B., et al., A Rachford-Rice Like Equation for Solvent Evaporation in the Bubble Electrospinning, *Thermal Science*, 22 (2018), 4, pp. 1679-1683
- [17] Yu, D. N., et al., Snail-Based Nanofibers, Mater. Lett. 220 (2018), June, pp. 5-7
- [18] Liu, Y. Q., et al., Nanoscale Multi-Phase Flow and its Application to Control Nanofiber Diameter, Thermal Science, 22 (2018), 1A, pp. 43-46
- [19] Tian, D., et al., Self-Assembly of Macromolecules in a Long and Narrow Tube, Thermal Science, 22 (2018), 4, pp. 1659-1664
- [20] Tian, D., et al., Strength of Bubble Walls and the Hall-Petch Effect in Bubble-Spinning, Textile Research Journal, 89 (2019), 7. pp. 1340-1344
- [21] Liu, P., et al., Geometrical Potential: an Explanation of Nanofibers Wettability, Thermal Science 22 (2018), 1A, pp. 33-38S
- [22] Tian, D., et al., Macromolecule Orientation in Nanofibers, Nanomaterials, 8 (2018), 11, ID 918
- [23] Tian, D., et al., Macromolecular Electrospinning: Basic Concept & Preliminary Experiment, Results in Physics, 11 (2018), Dec., pp. 740-742