

## ELIMINATION OF 4-NITROPHENOL FROM WATER BY OIL SHALE

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### Abstract

In this work, oil shale was used for elimination of a model potential anthropogenic pollutant, 4-nitrophenol. Sorption experiments were utilized under various different conditions; oil shale was pretreated with sodium azide to inhibit the microorganisms' activity, and the results were compared to those without pretreatment of oil shale. After a 24-hour equilibration time, in the presence of sodium azide pretreated oil shale, the concentration of 4-nitrophenol was higher than in the case of unpretreated oil shale, which indicates that during the sorption process not only sorption, but also decay of 4-nitrophenol took place. Desorption isotherm was also determined. Degradation experiments were applied to investigate how this persistent molecule transforms in the presence of oil shale. Sodium azide pretreated oil shale and MnCl<sub>2</sub> additive were also used to examine the effect of microorganisms and manganese(II) ion on the transformation of 4-nitrophenol. It was found that the presence of manganese(II) ion speeded up, while the sodium azide slowed down the transformation of the model molecule.

### Introduction

Oil shale is a lamellar, sedimentary rock, its organic content can slightly be extracted by generally used organic solvents, but heat convection promotes this organic content to transform to oil. It consists of fossil algae biomass, clay mouldered from trap-tuff, volcanic wreckage and organic materials [1]. Application of oil shale is diverse: 1. in agriculture it is used as soil-ameliorating agent, starter fertilizer; 2. its curative power is utilized at some rheumatic diseases; 3. its considerable sorption ability can be applied for elimination of chemical compounds. Oil shale has already been used for acceleration of the degradation process of persistent molecules [2]. Distinguishing the location of formation of oil shale, two types occur in Hungary: laguna- and maar type.

4-nitrophenol can be utilized in multitudinous sectors in the industry as a precursor or intermediate of explosives, dyes, pesticides, pharmaceutical drugs. Since 4-nitrophenol is persistent, it can accumulate in soils and waters. It is listed as a priority pollutant material by Superfund sites. Only advanced chemical procedures and some bacteria can be used for degradation of 4-nitrophenol, such as Fenton, ozonation, electrochemical, photocatalysis, various nanoparticles and Pseudomonas bacteria [3-4]. In this work a simple procedure is presented, wherewith 4-nitrophenol can be easily eliminated, using Hungarian oil shale, a low-cost material.

### Experimental

Maar type oil shale (collected from Pula, Hungary) was used. It was ground to the size of  $\varnothing < 800 \mu\text{m}$ . 4-nitrophenol and manganese(II) chloride tetrahydrate were purchased from Reanal Laborvegyszer Kft., calcium chloride dehydrate and sodium azide were obtained from Lach-Ner s.r.o. and Merck Darmstadt, respectively. All chemicals were used without further purification. Concentration measurement of 4-nitrophenol was performed by Merck Hitachi HPLC with UV detector at 317 nm. A mixture of 30% methanol and 70% water (pH was set

by acetic acid to 4.6 value) was used as eluent at a flow rate of 1 mL/min. Radelkis combination pH electrode was used for pH measurement.

#### *Sorption on oil shale powder*

Sorption experiments were performed using 250 mL stoppered Erlenmeyer flasks, wherein 5 g of oil shale were weighed. 5 mL distilled water or solution of sodium azide (10 g/L) was poured on the oil shale and was left to swell overnight. Solution of various concentrations of 4-nitrophenol (10  $\mu\text{mol/L}$  to 20 mmol/L) were prepared, using 0.01 mol/L calcium chloride solution (pH=7.6). 50-50 mL of solutions were transferred to the swollen oil shale samples, and these suspensions were shaken and left to stand for 24 hours, until the equilibrium obtained. In order to separate the liquid and solid phases, approximately 2 mL of supernatant was sampled into an Eppendorf tube and centrifuged at 15000 rpm for 20 minutes. After centrifugation, concentration of 4-nitrophenol was measured by HPLC-UV.

#### *Desorption on oil shale powder*

The initial steps of desorption procedure were identical with the above mentioned method. Starting concentration range of 4-nitrophenol was 10  $\mu\text{mol/L}$  to 500  $\mu\text{mol/L}$ , solution of sodium azide was used for swelling of oil shale. After sorption equilibrating time (24 hours), the supernatant and oil shale were separated by centrifugation at 6000 rpm for 20 minutes. The removed supernatant (approximately 42 mL) was refilled by 0.01 mol/L calcium chloride solution. This suspension was shaken and left to stand another 24 hours. The supernatant was sampled and concentration of 4-nitrophenol was determined by HPLC-UV. The previous steps were repeated after 48 hours, the desorption process was completed.

#### *Degradation in the presence of oil shale powder*

25 g of oil shale powder was weighed into stoppered, 720 mL-glass flasks, and the oil shale was swollen by 25 mL of distillate water or solution of sodium azide (using 5, 10, 20 or 40 g/L concentration) or solution of manganese(II) chloride (30.4 g/L). Onto these swollen oil shale, 500  $\mu\text{mol/L}$  of 4-nitrophenol in 0.01 mol/L calcium chloride solution was added. This suspension was shaken and left to stand for 24 hours. After equilibration, a small amount of supernatant was sampled, centrifuged at 15000 rpm for 20 minutes, and the concentration of 4-nitrophenol was determined by HPLC-UV. The remained sampled supernatant was added to the original system. The degradation process was considered from this point. Samples were taken periodically and the concentration of 4-nitrophenol was measured.

In all cases, blank sample was applied and all samples were in triplicate.

### **Results and discussion**

Adsorption and desorption isotherms were analyzed in terms of Langmuir or Freundlich isotherm equation, whichever fits on the data better.

$$\text{Langmuir isotherm: } q_e = Q \cdot \frac{K_L \cdot c_e}{1 + K_L \cdot c_e}$$

$$\text{Freundlich isotherm: } q_e = K_F \cdot c_e^n$$

where  $q_e$  is the adsorption capacity at equilibrium (mol/g);  $c_e$  is the equilibrium solution concentration (mol/L);  $Q$  is the maximum amount of solute adsorbed for monolayer coverage of the surface (mol/g);  $K_L$  is the Langmuir constant (L/mol);  $K_F$  ( $\text{L}^n/(\text{mol}^{(n-1)} \cdot \text{g})$ ) and  $n$  are the Freundlich constants.

Degradation curves were constructed as zero or first order kinetics, whichever fits on the data better.

A comparison of adsorption isotherms of 4-nitrophenol on oil shale with and without pretreatment of sodium azide can be seen in Figure 1. In the case of oil shale pretreated with sodium azide, the extent of adsorption is slightly lower than for that without pretreatment. Sodium azide inhibits the microorganisms' activity in the oil shale, thus it can be concluded that in the case of oil shale without sodium azide, microorganisms in the oil shale trigger a small degree of degradation of 4-nitrophenol during the one-day sorption process.

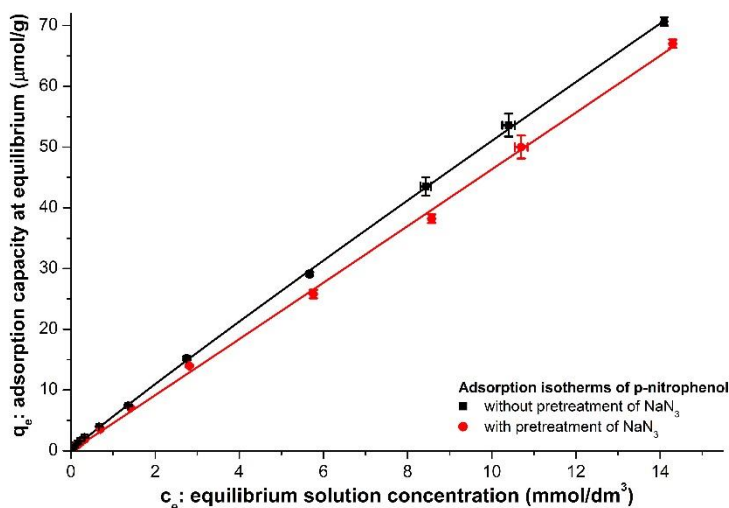


Figure 1. Adsorption isotherms of 4-nitrophenol

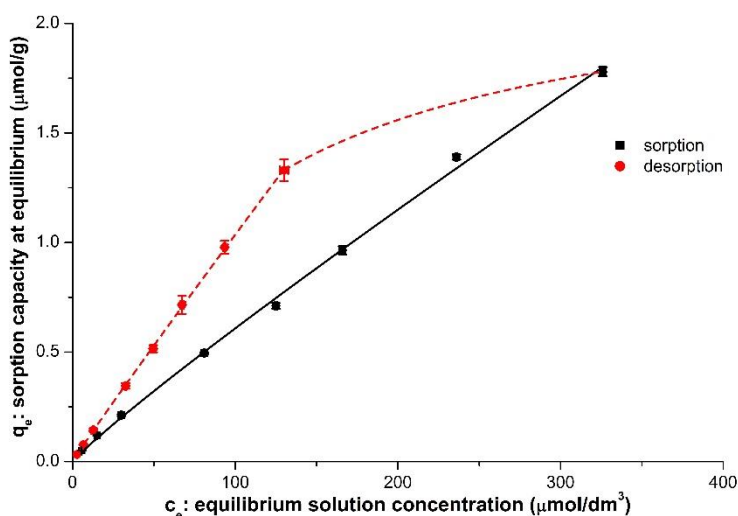
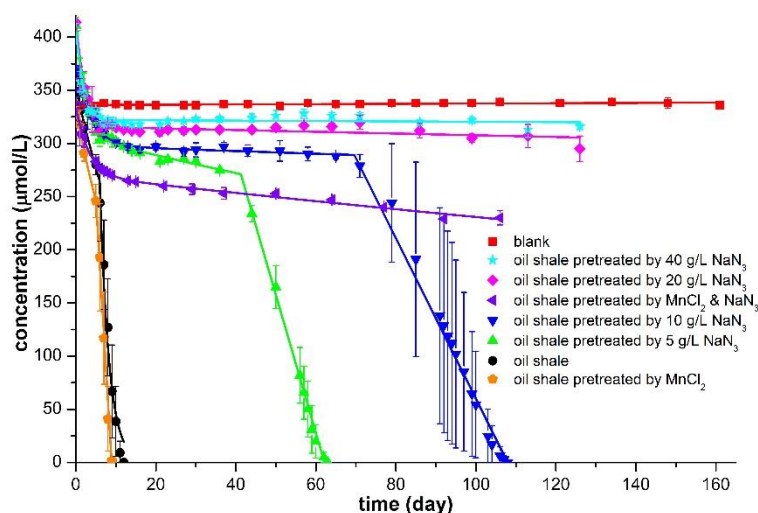


Figure 2. Adsorption-desorption isotherms of 4-nitrophenol

The hysteresis of adsorption-desorption isotherms can be seen in Figure 2. The nanoporous structure of oil shale containing kerogen caused a slow and reduced degree of desorption of 4-nitrophenol compared to the adsorption. After sorption of solute in kerogen, the desorption process was slow and retarded.



**Figure 3.** Degradation of 4-nitrophenol under various conditions

Figure 3. demonstrates the degradation of 4-nitrophenol. In the presence of oil shale, 4-nitrophenol transformed completely within 12 days. When oil shale was pretreated with sodium azide used in various concentrations, the time of degradation considerably increased because the microorganisms' activity was inhibited in the oil shale. When concentration of 5 g/l of sodium azide solution had been used, the transformation time of 4-nitrophenol was 63 days. In the case of 10 g/l, the transformation time changed to 108 days. When the concentration of sodium azide solution was increased to 20 and 40 g/l, the transformation time was much more than 130 days. These results highlight the importance of microorganisms' activity in the degradation process.

The effect of manganese(II) ions addition to the oil shale was the opposite, the time of the degradation of 4-nitrophenol decreased to 9 days. The difference between 9 and 12 days is not too large, but somehow the manganese(II) ions stimulate the microorganisms in the oil shale. It is proved by the experiment when the degradation of 4-nitrophenol was investigated in the presence of sodium azide pretreated oil shale, which contained manganese(II) ions. In this case, the time of the degradation of 4-nitrophenol was much more than 12 days, thus without microorganisms' activity, the effect of manganese(II) ions on degradation of the model compound was not favorable. A reasonable explanation can be given after the accurate identification of microorganisms.

We can notice breakpoints on the curves, which means that at least two consecutive processes are responsible for the transformation.

The analysis of the degradation product(s) of 4-nitrophenol is in progress.

### Conclusion

Oil shale, a low-price rock is a suitable material for elimination of environmental pollutants, such as 4-nitrophenol, utilizing its good sorption capacity and capability of degrading molecules, even if they are persistent. The importance of microorganisms content of oil shale at degradation process was denoted, and improvement of this process could be achieved by adding manganese(II) ions to the oil shale. Further investigation is necessary to thoroughly understand the mechanism of the transformation.

### **Acknowledgements**

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### **References**

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