

HORIZONTAL PERMEABLE REACTIVE BARRIERS FOR GROUNDWATER RECHARGE WITH WASTEWATER: KINETICS AND ADSORPTION ASSAYS.

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Abstract

Permeable Reactive Barriers (PRB) are widely used to eliminate pollutants from groundwater. Another possible use of PRB is the regeneration of treated wastewater for aquifer recharge, as it is listed in the Royal Decree 1620/2007. Kinetics and adsorption assays have been performed previously to the construction and installation of a horizontal Permeable Reactive Barrier, in order to evaluate the sorption capacity of activated carbon, zeolite, palygorskite and peat in the removal of different substances still present in treated wastewater. As for the sorption equilibrium, Langmuir and Freundlich equations has been applied to data. In general, Freundlich isotherm shows a better fit. Regarding the kinetics studies, zero, first and second order, pseudo-first and second order and parabolic diffusion equations have been tested, showing the pseudo-second order the best results. The results with the different reactive materials point to a selective adsorption, allowing such a regenerated water quality that it will not deteriorate the groundwater quality.

Keywords: sorption, Horizontal Permeable Reactive Barrier, isotherms, kinetics, recharge and regeneration

Introduction

The Permeable Reactive Barrier (PRB) technology is defined by the US-EPA as a passive "in situ" treatment zone made up by reactive materials which transform or retain contaminants when water flows through them (EPA, 1998). The PRB technology has been applied to a wide range of contaminants, both organics (eg. organochlorines) and inorganics (eg. phosphates and nitrates). Besides, it is considered as one of the most viable 'green' alternatives due to their cost - results ratio in "in situ" soil and groundwater decontamination, being its application suitable for wastewater treatment in small communities. In this project, a horizontal PRB made of activated carbon, zeolite, palygorskite and peat is being studied for the regeneration of urban wastewater for aquifer recharge, one of the uses referred to in the Royal Decree 1620/2007. The barrier will be installed in a research plot located at the Experimental Wastewater Treatment Plant of Carrión de los Céspedes (PECC) (Seville – Spain). There, non-conventional wastewater treatments and their applicability and development in small towns are studied. The main aim of this study is to investigate the capacity of the four reactive

materials to remove the different substances still remaining in the treated wastewater (de Bustamante *et al.*, 2009) in order not to diminish the groundwater quality when carrying out the aquifer recharge.

Methods

The wastewater used in this study has been obtained from the PECC. It was taken after passing through a secondary treatment. Both, sewage effluent and groundwater have been characterized through periodic sampling in order to meet the critical parameters of the effluent, which must be reduced with the horizontal PRB before water reaches the aquifer. To date, treatment experiment has been carried out using batch essays (adsorption isotherms and kinetics) through the addition of activated carbon, zeolite, palygorskite or peat to the treated wastewater. Prior to application as adsorbents, the materials have been washed with milliQ water and oven dried at 105 °C for 24 h. For both tests, a constant wastewater volume of 400 ml was used. The adsorbent amount was varied from 1:4 to 1:84 in sorption assays and was kept constant (1:4) in the kinetics ones. To facilitate the mass transfer process, the flasks were shaken at 140 rpm at 25 °C ± 2 °C for 24 h in adsorption tests. In kinetics experiments, the reaction was stopped at different times. In both cases before analyses, the samples were filtered through vacuum and with 0,45µm nylon filters in order to remove the adsorbent particles remaining in the water.

Results and discussion

After comparing sewage effluent and groundwater physico-chemical properties, seven critical parameters have been determined as critical factors for a special follow-up: COD, TOC, NO₃⁻, NO₂⁻, PO₄³⁻, NH₄⁺ and K⁺ (Table 1). Values in treated wastewater effluent overcome the groundwater values as much as 400%.

Table 1. Characteristical groundwater and treated wastewater effluent parametres.

	Treated Wastewater Effluent	Groundwater
COD (mg/l)	55.15	<0.4 – 15.4
TOC (mg/l)	22.2	<0.5 – 5.7
NO ₂ ⁻ (mg/l)	0.5	N.D.*
NO ₃ ⁻ (mg/l)	177.9	N.D. – 7.01
PO ₄ ³⁻ (mg/l)	2.75	N.D.
NH ₄ ⁺ (mg/l)	30.35	N.D. – 2.3
K ⁺ (mg/l)	19.90	N.D. – 10.6

*N.D. → Non Detected

Table II. Sorption and kinetics parameters for the adsorption of contaminants in different reactive materials.

		Sorption Isotherms				Kinetics				
		Freundlich		Langmuir		Pseudo-second order				
		n	K_F (mg/g)(L/g) ^{1/n}	R ²	b (mg/g)	K_L (L/mg)	R ²	k ₂ (1/h)	q _e (mg/g)	R ²
Activated Carbon	NH ₄ ⁺	2,743	3,36·10 ⁻²	0,737	0,187	5,52·10 ⁻²	0,880	12,610	0,098	0,942
	Na ⁺	0,523	4,60·10 ⁻⁴	0,991	-0,589	-1,17·10 ⁻²	0,943	5,461	0,196	0,985
Zeolite	NH ₄ ⁺	1,009	1,83·10 ⁻¹	0,985	0,701	8,77·10 ⁻²	0,980	12,397	0,088	0,510
	K ⁺	0,832	7,45·10 ⁻³	0,894	-0,564	-1,72·10 ⁻²	0,219	17,694	0,057	0,999
Palygorskite	NH ₄ ⁺	1,668	8,04·10 ⁻²	0,995	0,701	8,77·10 ⁻²	0,980	6,715	0,152	0,998

In general, Freundlich isotherm shows the best fit (Table II). As for the rest of critical parameters, NO₂⁻ and NO₃⁻ are completely eliminated after the treatment with activated carbon, zeolite and palygorskite, preventing their fit to kinetic and adsorption models. The COD and TOC with 9.4 and 0 mg/l values, respectively, reached the target range after activated carbon wastewater treatment. Similarly, is the case of peat, activated carbon and zeolite for PO₄³⁻. Regarding the equilibrium time, all the reactives but zeolite reach it before 10 hours of reaction (an example is given in Figure 1).

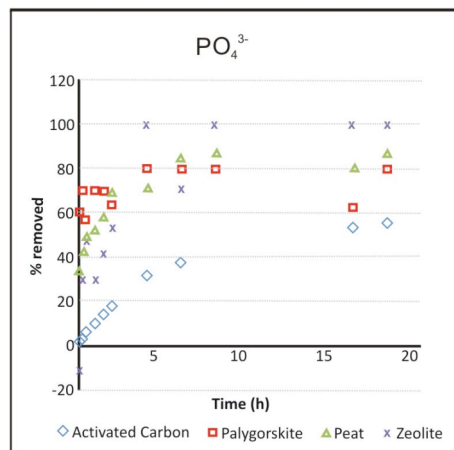


Figura 1. PO₄³⁻ removal evolution for the studied reactive materials.

Conclusions

The studied materials are selective about the sorption of analytes from treated wastewater. Activated carbon is the most effective material in terms of COD and TOC elimination, two of the critical parameters identified in the characterization of the studied area. Zeolite eliminates fast 100% of PO_4^{3-} . Due to its cationic exchange behavior, palygorskite reduces NH_4^+ and K^+ . As for the peat, the best results with it are expected to be obtained in continuous kinetic essays, when microbial activity can be developed. The results point out that the removal of NO_2^- and NO_3^{2-} should not be a problem since they are quite well removed with the four studied materials. Thus, the overall results suggest that the effluent of horizontal-PRB will reach the analyte-concentrations measured in the aquifer in less than 10 hours of contact time, so the groundwater quality will not be deteriorated. However, the continuous kinetic assays are essential to know better the removal performance of the reactive materials.

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