THE USE OF PERMEABLE REACTIVE BARRIERS FOR REMOVAL OF PHOSPHATE FROM GROUND WATERS

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Abstract:Permeable reactive barriers represent a promising remediation method for surface and groundwater containing a variety of inorganic and organic pollutants. Phosphate is a nutrient which leads to an extensive water eutrophication. It can be removed from surface and ground waters by means of permeable reactive barriers after using precipitation or adsorption. The aim of this study was to evaluate the permeable reactive barriers efficiency in the case of phosphate removal from groundwaters.
In this paper, clay mold soil type was used as a reactive permeable matrix for ground water phosphate removal. Also, the influence of the main operational parameters, namely: pH, initial solution concentration and contact time on the thermodynamic system behavior was investigated. The experimental results obtained were interpreted with the help of Temkin and Flory-Huggins adsorption isotherms.
Keywords : phosphate removal, permeable reactive barriers, groundwater remediation, adsorption isotherms

1. INTRODUCTION

Between 1982 and 1997 for groundwater treatment only surface techniques were applied. The groundwater surface treatment technology is a major energy consumption source and can not remove the contaminants adsorbed on the soil. As a result of the researches, an in situ passive treatment method was discovered named "barrier/permeable and reactive treatment area". [1,2]

In 1998, USEPA defined it as being:" a site of the underground containing a reactive material, designed to intercept the pollution plume, to ensure the flow of the plume through the reactive medium and for transforming the pollutants into less harmful compounds, from the environmental point of view."[3]

Currently, permeable reactive barriers are some of the most promising technologies for passive treatment of the groundwater due to high retention efficiency of different contaminants and low price compared to other *in situ* technologies. [4]

A typical configuration of the permeable reactive barriers is presented in figure 1. The chemical compounds which are retained in the permeable reactive barriers are either broken down into other compounds less hazardous or are effectively fixed on the reactive material. [5]

A variety of pollutants are degraded, precipitated, adsorbed, or change in the reactive area, including chlorinated solvents, heavy metals, radionuclides and other inorganic or organic species.

In general, the mechanism by which the groundwater is treated consists into its direct passage through the reactive area of the permeable reactive barriers where contaminants are either immobilized or chemically transformed. [6]

The permeable reactive barrier (PRB) acts as a barrier, not for water, but for the compounds which are generating contamination. The pollutants removal takes place in two ways:

- by introducing an adsorption medium for the contaminants;

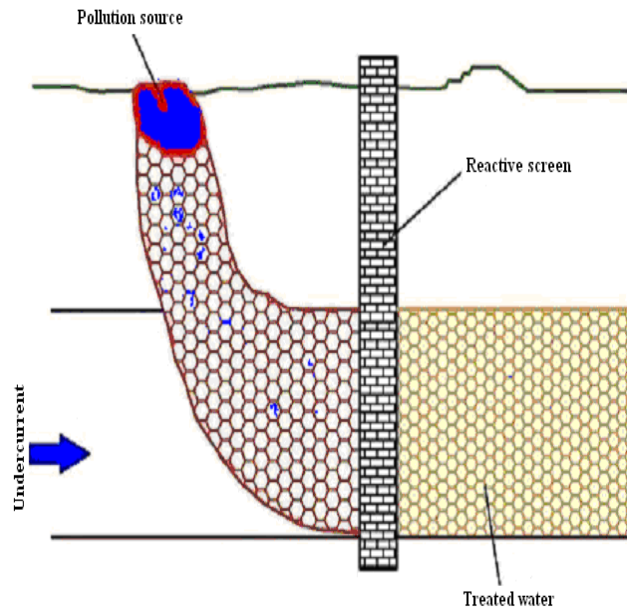- by introducing a medium which will alter the contaminants and reduce their bioavailability.[7]

Figure 1: Permeable reactive screen configuration [8]

This fact can be achieved both by changing the speciation and by provision of a ligand with which to form a solid. The second version was more often used simply because the adsorbent surface quickly saturates, leaving the contaminants unchanged and thus, the barriers permeability is reduced. The contaminant is transformed into a harmless form by changing its oxidation state. The main configurations of reactive barrier systems are: [9]

- continues barriers;
- "funnel-gate" type systems;
- walls filled with reactive material systems;
- injection systems.

For the construction of a permeable reactive barrier several types of reactive materials can be used:

- granular metals: Al, Zn, Cu, stainless steel, but especially iron are the most used materials in laboratory facilities, at pilot or large scale;
- granular iron with amendments;
- bimetallic materials.

The choice of material for reactive barriers is governed by the following considerations:

- reactivity: are preferred the materials which provide lower half-times (greater degradation rate);
- stability: the time period during which the maintains its reactivity;
- availability and cost: cheap materials are preferred as against the expensive ones, especially when the performances differ only slightly;
- compatibility with the environment: reactive material must not introduce dangerous byproducts into the environment;
- security: the material must not endanger the safety and health of workers. [10]

2. MATERIALS AND METHODS

2.1. Working procedure

All the reagents used for the present study were analytical grade and purchased from Merck. The experiments were performed on clay mold soil type samples, at 20 ° and a soil: solution phase mass ratio of 1: 5. The mobile phosphorus amount (expressed as phosphate) was determined according to the procedure described in SR 11411-2: 1998. During the thermodynamic study, the soil samples were left in contact with a KH_2PO_4 solution having the following concentrations: 10, 20, 40, 60, 80, 100 mg/L for 24 hours in order to achieve equilibrium. The

water-soil suspension was vacuum filtered. From the resulting aqueous extract 10 mL were pipetted in a volumetric flask in which were added 12.5 ml of vanadomolybdenum reactive and brought to 50 mL with distilled water. The samples obtained were spectrophotometrically analyzed at a wavelength of 470 nm.

2.2. Soil sample characterization

The clay mold soil type (argillic) used in this study comes from the Urziceni city. An important characteristic of the county is that on an area not very large are succeeding: carbonate chernozem, chernozem itself, cambic chernozem, argillic chernozem and typical reddish brown soil, the last one present in small areas in the extreme west of the county.

These soils have high fertility thus allowing the widespread practice of agriculture, predominant being the grain crop production. The main physico-chemical properties of clay mold soil type are presented in table 1.

Table 1: The physico-chemical properties of clay mold soil type [4,11]

Property	Value	Analysis method
pH	7,85	SR ISO 1039:1999
Humus (%)	2,00	STAS 7184/21-82
$CaCO_3$ (%)	0,00	STAS 7184/16-80
Macroelements		
N_{total} (%)	0,12	SR ISO 11261:2000
P_{AL} (mg/kg)	20,00	STAS 7184/19-82
P_{total} (%)	0,065	STAS 7184/14-79
K_{AL} (mg/kg)	12,00	STAS 7184/18-80
Microelements		
Zn (mg/kg)	80,20	SR ISO 11047:1999
Cu (mg/kg)	27,40	
Pb (mg/kg)	21,70	
Co (mg/kg)	9,70	
Ni (mg/kg)	55,80	
Cr (mg/kg)	13,20	
Cd (mg/kg)	0,01	
Fe (mg/kg)	256,71	SR ISO 6332:1996
Al (mg/kg)	295,00	STAS 6326-90

Note: The soil characterization was done and offered by Agrochemistry and Pedology Research Institute (ICPA) Bucharest

3. RESULTS AND DISCUSSIONS

Phosphate transformations in the soil reactive permeable barrier must be done analytically on components and overall synthetic, because this is the only way that allows us to study the intimate mechanisms and interactions that occur and regulates soil retention processes.

Soil, as a poly-dispersed, heterogeneous system with three phases (solid, liquid, gas) tends to achieve a state of dynamic equilibrium that changes depending on the environmental factors mode of action (climate, plants, crop technique).

The relationships that exist between the solid and liquid phase reflects phosphate dynamics both through physical and chemical mechanisms. [1,12]

3.1. Temkin model

The thermodynamic study of the phosphate removal from groundwaters by means of permeable reactive barriers use aimed to determine the maximum soil adsorption capacity for this pollutant based on the experimental data obtained.

The data were interpreted using classical adsorption models, namely Temkin and Flory-Huggins. [13]

In the case of Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. [14,15]

The equation used for describing Temkin isotherm is:

$$q_e = \frac{RT}{b} Ln(K_T C_e) \tag{1}$$

By linearization, equation (1) becomes:

$$q_e = B_T \ln K_T + B_T Ln C_e \qquad (2)$$

where: T = the absolute temperature (K), R = universal gas constant (8.314 J/molK), K_T = equilibrium binding constant (L/mg), b_T = variation of the adsorption energy (kJ/mol), B_T = Temkin constant related to the heat of adsorption (kJ/mol).

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates.

In figure 2 are presented the adsorption isotherms achieved for the experimental data obtained for two working solution initial pH values (5 and 7), as well the theoretical adsorption isotherms obtained based on the Temkin model.

From the data presented it can be observed that the initial pH value has an influence on the phosphate removal through adsorption mechanisms, the adsorption capacity (q_e) at pH = 5 being with 10% higher than the one obtained for pH = 7.

Also, the graphical representation reveals the fact that experimental data are well fitted by the curves obtained using Temkin model.
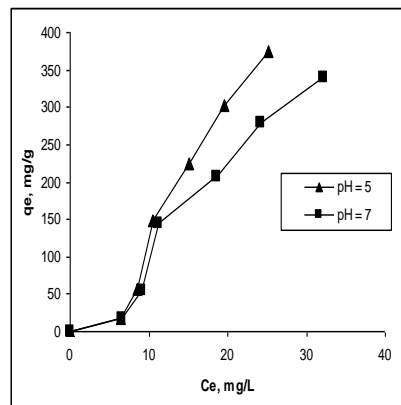
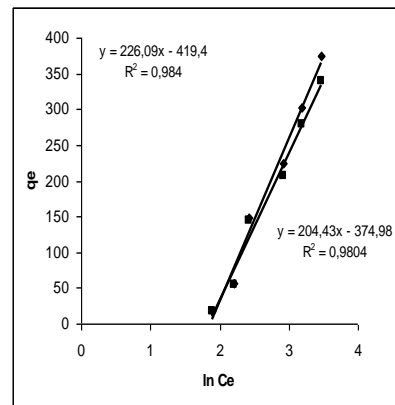| **Figure 2:** Adsorption isotherms for Temkin model	**Figure 3:** Graphical representation of the linear form for Temkin equation, pH 5 (▲), pH 7(■)

The results presented in figure 3, revealed that the correlation coefficients (R^2) obtained for two data sets have values higher than 0.97, fact which suggests that the phosphate adsorption equilibrium on the permeable reactive barrier can be described by means of Temkin model. [15]

Table 2: Temkin parameters

Initial pH value	B_T	K_T
5	10,04	0,156
7	11,10	0,159

From the data presented in Table 2, resulted that Temkin adsorption potential K_T, had a very low value (0.15) fact that clearly reveals a very low potential of the reactive barrier for the phosphate ion. Regarding Temkin constant, b_T, related to heat of phosphate sorption the values were higher than 10 kJmol^{-1}. According to the literature, the typical range of bonding energy for ion-exchange mechanism is 8-16 kJ mol^{-1}. The values relatively low obtained for this parameter indicates a relatively weak interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study. [16]

3.2. Flory-Huggins model

This mathematical model was chosen in order to determine the surface coverage degree characteristics of the adsorbate on the adsorbent. The linear form of the Flory-Huggins equation can be expressed as follows:

$$ln\left(\frac{\theta}{C_0}\right) = ln K_{FH} + n\,ln(1-\theta) \qquad (3)$$

where: $\theta = (1-C_e/C_0)$, the degree of surface coverage, n = number of phosphate ion occupying adsorption sites, K_{FH} = the equilibrium constant (L/mol). [17, 18]
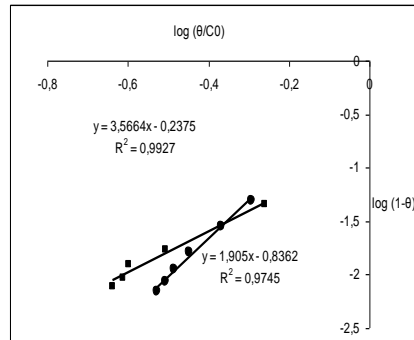
Figure 4: The linear form of Flory-Huggins equation representation, pH 5 ($\bullet$), pH 7($\blacksquare$)

In figure 4 is represented the linear form of Flory-Huggins equation for experimental data obtained at pH=5 and pH =7.

From graphical representation analysis we can affirm that better results are obtained in the case of pH = 5, corresponding to a correlation coefficient (R^2) higher than 0.99, compared to 0.97 obtained in the case of initial solution pH = 7.

A value of R^2 higher than 0.97 suggest that the phosphate adsorption during the interaction with the permeable reactive barrier can be also described using Flory-Huggins model.

4. CONCLUSION

The aim of this study was to evaluate the permeable reactive barriers efficiency in the case of phosphate removal from groundwaters. Different permeable reactive mixtures can be used for phosphate removal. Mixtures can be placed in situ, as horizontal or vertical reactive barriers in sediments receiving wastewaters, or can be used in a single pass, as self-contained treatment modules in the alternative treatment systems. The thermodynamic system behavior was investigated. The experimental results obtained were interpreted with the help of Temkin and Flory-Huggins adsorption isotherms. The first conclusion that resulted after the study was that the use of a permeable reactive barrier made from a mold clay soil containing metal oxide responsible for adsorption (e.g. iron oxides, alumina), a calcium source for precipitation (limestone, $CaCO_3$) for ground water phosphate removal lead to satisfactory results. The second conclusion was that the values relatively low obtained for b_T indicates a relatively weak interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study.

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