

Eutrophication decrease: phosphates reduction in presence of nitrates by adsorption processes

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ABSTRACT

Eutrophication is a process in which a water body is enriched in soluble nutrients stimulating the aquatic growth resulting in the depletion of dissolved oxygen. This phenomenon causes aquatic environment degradation as well as serious problems for different purposes of waters use.

Phosphorus and nitrogen, under mainly phosphate and nitrate chemical species, are considered responsible for eutrophication degradation.

The main purpose of this research was to study, at laboratory scale, different processes based on adsorption mechanisms for decreasing the concentration of phosphates in presence of nitrates in natural waters. The study was focused on dolomite (sedimentary rock), hydroxyapatite (bone meal) and slag as adsorbents.

Dolomite and hydroxyapatite showed a high capacity for phosphate adsorption even in presence of nitrate. The results of the experiments with slag as adsorbent were low in terms of removal capacity and they not showed a clear trend.

Further studies will include experiments in continuous reactors with the ultimate goal of designing a low-cost process to help decrease waterways eutrophication.

KEYWORDS

eutrophication, phosphates, nitrates, adsorption, dolomite.

INTRODUCTION

Eutrophication of water bodies caused by the increased amount of nutrients has become a problem throughout the world [1]. This phenomenon produces aquatic environment degradation, as well as a serious problem for different purposes of water uses [2-4].

Nitrogen and phosphorus are two key elements responsible for the excessive increase of nutrients inducing algae and other aquatic plants growth. Although algae production is needed as a first link in the food chain of aquatic ecosystem, excessive growth under eutrophic conditions could eventually lead to a significant deterioration of the water body. Therefore, the first step for eutrophication acceleration is the entry of these nutrients in the aquatic system [5].

Phosphorus is an element that occurs naturally in water, however, certain human activities contribute significantly to its accumulation in water bodies. According to Von Sperling [6], the natural origin of the phosphorus compounds may be in the dissolution of soils compounds, in the decomposition of organic matter and in the cellular decomposition of microorganisms;

its anthropogenic source is related to domestic and industrial wastes, detergents, and animal excrement and fertilizers.

In the environment, the high concentration of nitrogen, as nitrates, not only favours the eutrophication of water bodies, but also produces very important implications for public health. The high nitrate concentration in drinking water is the main cause of methemoglobinemia. Nitrates can be reduced to nitrites by intestinal bacteria and pass to the blood, producing the oxidation of Fe(II)-haemoglobin and making methaemoglobin unable to bind and carry oxygen to tissues [7].

The purpose of this work was to study, at laboratory scale, processes allowing to decrease phosphate and nitrate concentrations by adsorption processes.

Adsorptive processes have great potential as new technologies. They are characterized by the use of cheap materials, non-toxic, biodegradable and reusable in some cases [8-10]. Furthermore, these adsorption methods have proven being useful for removing phosphates and nitrates in surface waters. Different combinations of contaminant/adsorbent under various experimental conditions have been extensively studied [11]. These methods are particularly suitable for treatment of contaminated natural waters [12- 14].

The adsorbents selection was made taking into account their low costs and possibilities of reuse. This study was focused on dolomite (sedimentary rock), hydroxyapatite (bone meal) and slag. Dolomite is a mineral that can be found in sedimentary layers several hundred feet thick, which is also found in metamorphic marbles, hydrothermal veins and replacement deposits. The general formula is $AB(CO_3)_2$, wherein A can be calcium, barium or strontium and B can be iron, magnesium, zinc or manganese. Hydroxiapatite ($Ca_5(PO_4)_3(OH)$) is the major inorganic component of bone tissue of vertebrates. Slag is a by-product of smelting ore to purify metals, is a mixture of metal oxides as lime (CaO), silica (SiO_2), alumina (Al_2O_3), magnesia (MgO), and sulfides.

In this study, these adsorbents are tested for treatment of water with phosphates and nitrates. Kinetics studies are performed to better understand these processes.

MATERIALS AND METHODS

The phosphorous concentration was determined according to the molybdovanadate method. Nitrate concentration was determined using a ion selective electrode [15].

Dosage curves were performed in batch mode in order to optimize the amount of adsorbent mass for removal phosphate and nitrate ions from a defined solution. For this purpose, different masses of the adsorbents were in contact with 50 mL of a solution containing 30 mg phosphate/L or 40 mg nitrate/L, at $pH = 7.0 \pm 0.2$. The systems were shaken at 200 rpm, for 24 hours, at $25 \pm 2^\circ C$.

The experimental data for the adsorption isotherms were performed measuring the residual concentration at equilibrium state (after 24 h) obtained from systems with different masses of adsorbents with a constant concentration of phosphate (30 mg/L) and the same volume of the solution (50mL).

The kinetic studies of the adsorption process were performed measuring residual concentration at different times. The equilibrium times were defined when residual concentrations remain constant.

All experiments were performed, at least, in triplicate.

To study the experimental data of adsorption experiments, Langmuir and Freundlich models were employed. The proposed equation by Langmuir [16] applies to both, physical and chemical adsorption, and can be used to describe the equilibrium conditions for different adsorbate/adsorbent systems. The linear Langmuir equation is given by:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (1)$$

where, q_e (mg/g) is the amount of adsorbed species per unit mass of adsorbent at the equilibrium state, C_e (mg/L) is the concentration of the solution at the equilibrium state, q_m (mg/g) and b (L/mg) are Langmuir constants related to the maximum capacity and energy of adsorption, respectively.

The Freundlich model [17] assumes that the adsorption should be purely a physical process without change in the configuration of molecules. The linear equation which describes this model is presented below:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where, K_f and n are parameters related to the adsorption capacity and intensity, respectively. For fitting experimental data obtained in the kinetic assays, pseudo-first order and pseudo-second order models were employed.

The mathematical expression for the kinetics of pseudo-first order [18] is widely used for adsorption studies of liquids. The linear form is:

$$\ln(q_e - q_t) = \ln q_e - k t \quad (3)$$

where q_t is the amount of adsorbed solute (mg/g) at time t , and k (min^{-1}) is the constant velocity.

The pseudo-second order model was developed by Ho and McKay [19]. It is assumed that sorbate is adsorbed on two active sites on the sorbent. The process can be expressed in a linear form by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (4)$$

where, k_s (mg/g min) is the velocity constant of pseudo-second order. The term $(k_s q_e^2)$ represents the initial adsorption rate.

For obtaining the fitting parameters, OriginPro 8.5.1® software package was used.

RESULTS AND DISCUSSION

Dosage curves

In Figure 1, the dosage curves for phosphate and for phosphate in presence of nitrate on dolomite, hydroxiapatite, and slag, are presented, respectively.

For the three studied adsorbents, the amount of adsorbed phosphate increased with the adsorbent mass. However, for none of the three adsorbents nitrate adsorption was observed. It must be noted that the presence of nitrate does not modify the amount of adsorbed phosphate neither onto dolomite nor hydroxyapatite. The higher removal percentage for phosphate was obtained using hydroxiapatite systems while the lower was with slag systems. The experimental adsorption capacities (q_{max}) for phosphate were 0.25 mg/g on dolomite, 1.2mg/g on hydroxiapatite and 0.07 mg/g on slag. It must be noted that both, dolomite and hydroxyapatite, showed high capacity for phosphate even in the presence of nitrate. The results of the experiments with slag as adsorbent were low in terms of removal capacity and they not showed a clear trend, confidence was lower than necessary for further conclusions.

Adsorption isotherms

Isothermal studies were done for systems with phosphate, and phosphate in presence on nitrate on dolomite and hydroxiapatite. The experimental data plotted in Figure 2, show the adsorption isotherms (removed adsorbate concentration per gram of adsorbent at equilibrium (q_e) vs the remaining adsorbate concentration in the aqueous solution (C_e)), onto dolomite and onto hydroxiapatite.

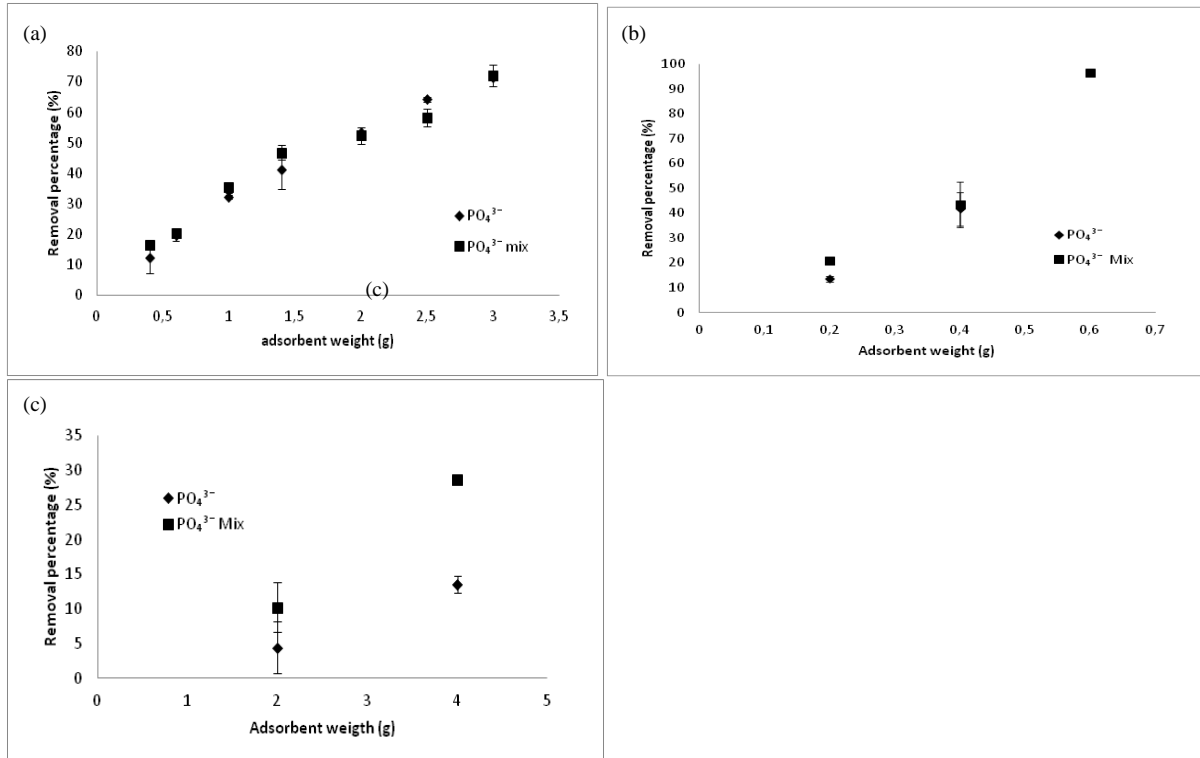


Figure 1: Dosage curves for phosphate and for phosphate in presence of nitrate on: (a) dolomite, (b) hydroxiapatite, and (c) slag.

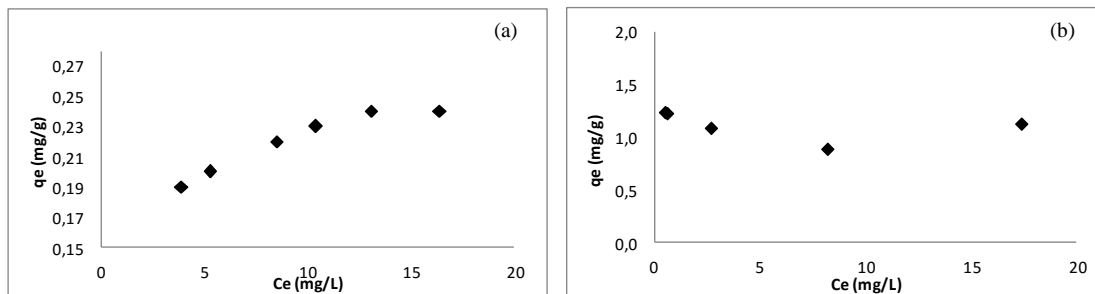


Figure 2: Adsorption isotherms form experimental for phosphate on a) dolomite, and b) hydroxiapatite.

According to Sepulveda et al [20], the shape of the adsorption isotherms, being convex or concave, could allow classify them as unfavorable or favorable, respectively. This is a general classification based on pure visual observation of experimental data (shape and curvature) for the adsorption isotherm [21]. In Figure 2, on dolomite, the adsorption process appear to be favorable, and for the hidroxapatite, unfavorable.

In Table 1, the parameters from the fitting of Langmuir and Freundlich models to the experimental data are shown.

The Langmuir model fits satisfactorily the experimental data from phosphate adsorption onto

both tested adsorbents. The q_m parameter (adsorption capacity) for dolomite is (0.27 mg of phosphate/g) lower than for hydroxyapatite (1.10 mg/g), both results are similar to the experimental values. The b parameter (related to the binding energy between the phosphate and the adsorbent) describe the same situation: it is more than ten times higher for hydroxyapatite-phosphate (3.53) than for dolomite-phosphate (0.30).

The Freundlich model fit satisfactorily only the experimental data from phosphate adsorption onto dolomite.

Table 1: Isotherm parameters for the adsorption of phosphate on dolomite and hydroxyapatite.

Adsorbent	Langmuir			Freundlich		
	$q_m(\text{mg/g})$	b	R^2	n	K_f	R^2
Dolomite	0.30	0.30	0.9923	3.21	0.10	0.9175
Hydroxyapatite	1.10	3.53	0.9828	17.7	1.17	0.4327

Adsorption kinetics

The kinetics of the phosphate adsorption process was studied using the pseudo-first and second order models. Satisfactory correlation coefficients were obtained with the second-order model. Graphics are shown in Figure 3 and obtained parameters in Tables 2 and 3.

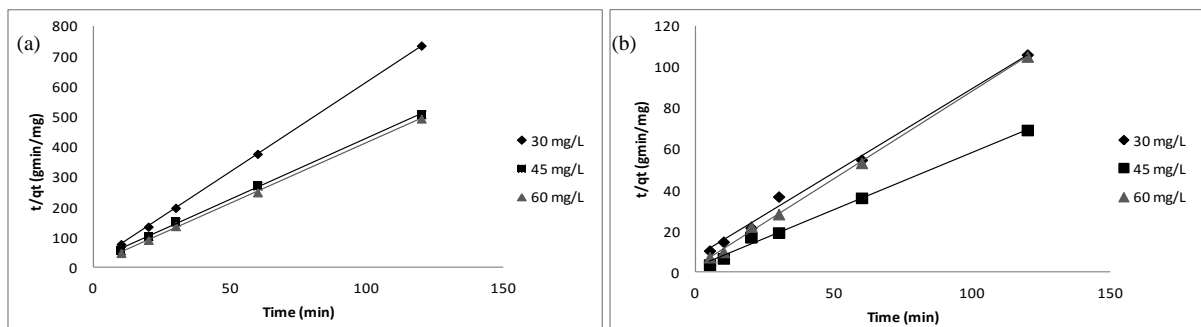


Figure 3: Experimental kinetics curves fitted to the pseudo-second order model for PO_4^{3-} on (a) dolomite, and (b) hydroxyapatite.

Table 2: Kinetics parameters obtained from the adsorption of phosphate onto dolomite.

Initial PO_4^{3-} concentration	$q_e(\text{exp.})$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		q_e (mg/g)	$k(\text{min}^{-1})$	R^2	q_e (mg/g)	k_s	R^2
30	0.17	0.034	0.0122	0.834	0.167	0.0021	1
45	0.24	0.077	0.0270	0.985	0.246	0.0007	0.9991
60	0.25	0.043	0.0193	0.863	0.248	0.0015	0.9996

Table 3: Kinetics parameters obtained from the adsorption of phosphate onto hydroxiapatite.

Initial PO_4^{3-} concentration	$q_e(\text{exp.})$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		q_e (mg/g)	$k(\text{min}^{-1})$	R^2	q_e (mg/g)	k_s	R^2
30	1.13	0.807	0.0496	0.9096	1.212	0.0959	0.9949
45	1.73	0.465	0.0287	0.6694	1.782	0.1283	0.9947

60	1.14	0.446	0.0562	0.8758	1.175	0.2468	0.9988
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For both adsorbents, the equilibrium time was achieved after 60 minutes.

The values obtained for R^2 show the ability of the pseudo second-order model to represent the experimental results to a higher degree of accuracy ($R^2 > 0.99$) in both systems. Besides, the q_e values calculated from the pseudo second-order model were close to the experimental values. It was found that the initial adsorption rate ($k_s q_e^2$) increases with the initial concentration. The non-linear relation between the rate constants and the initial concentrations indicates that both mechanisms such as ion exchange and physical adsorption are involved in the process [22].

CONCLUSIONS

Phosphate adsorption onto dolomite and hydroxiapatite was studied. It can be concluded that the presence of nitrate in the water to be treated, does not modify the results for removing phosphate. After this study, both adsorbents could be useful for water treatment with phosphates in presence of appreciable amount of nitrate.

Hydroxiapatite shows the best adsorption capacity for phosphate. Kinetics studies indicate that mechanisms such as ion exchange and physical adsorption are involved in the process.

These studies will pursue conducting experiments in continuous reactors with the ultimate goal of designing a low-cost process to help decrease waterways eutrophication.

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NOMENCLATURE

C_e	concentration of the solution at equilibrium state	[mg/L]
t	time	[min]
q_e	amount of adsorbed species per unit mass of adsorbent at the equilibrium state	[mg/g]
q_t	amount of adsorbed species per unit mass of adsorbent at the time t	[mg/g]
q_m	Langmuir parameter related to the maximum capacity of the adsorbent	[mg/g]
b	Langmuir parameter related to the energy of adsorption	[L/mg]
K_f	Freundlich parameter related to the adsorption capacity	
n	Freundlich parameter related to the intensity of adsorption	
k	velocity constant in the pseudo-first order model	[min ⁻¹]
k_s	velocity constant in the pseudo-second order model	[min ⁻¹]

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