Kinetic and equilibrium studies of phosphorous adsorption: Effect of physical and chemical properties of adsorption agent

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Keywords:

Phosphorous
Wastewater
Kinetics
Adsorption composition

Abstract

Several materials, with and without thermal treatment, were used as phosphorus removal agents. Surface area, porosity and chemical composition were determined for each material aiming to study their effect on phosphorus removal. While, calcined waste eggshell (ES) and natural crushed minerals (calcium (M1), iron (M2) and aluminum (M3)) were not sensible to pH variation, zeolites, USY and HY, exhibited a maximum removal above pH 4 . Laboratory adsorption experiments (72 h of equilibrium at 22°C and 200 rpm) using the different materials revealed a phosphorous removal ability of 26.48,0.14,0.14,0.11, 0.12 and 0.10mgPg^{-1} for ES, USY, HY, M1, M2 and M3, respectively. The adsorption revealed to be chemical for USY and HY and physical for the remaining materials. ES demonstrated to efficiently reduce the phosphorus concentration present in wastewater.

Introduction

All living organisms require essential nutrients, in particular phosphorus, for their growth, metabolism and reproduction (PenaPereira et al., 2011). Phosphorus, the 11th abundant element in crustal rocks of the earth, is predominantly found in the form of phosphate ($PO_4{}^{3-}$) and extensively used by many applications, being fertilizers and detergents the most important (Shyla and Nagendrappa, 2011). However, due to human activities, inadvertent addition of phosphates to freshwater bodies has caused eutrophication. A worldwide problem, that commonly occurs in stagnant water bodies (Oliveira et al., 2012; Søndergaard et al., 2013). In severe cases, it provokes oxygen depletion, which affects fish and other aquatic life, microorganism and insects' growth, as well as, it causes natural resorts degradation (Karageorgiou et al., 2007). Therefore, the removal of phosphates from eutrophic waters and reduction of its inputs are crucial.

Lately, physical, chemical and biological methods have been investigated to reduce phosphorus concentration in wastewater effluents (He et al., 2013). Lime, aluminum sulphate and ferric chloride are the more common chemicals used to precipitate phosphorus. Recycling and re-use of industrial and agricultural wastes as phosphorus adsorbents is environmentally friendly, and cost-effective. Coal fly ash, slag, red mud, alum sludge, cow bone, peat, oyster shell, scallop shell, wheat straw and iron oxide tailings have been used to remove phosphate (Barca et al., 2014; Wajima and Rakovan, 2013). Nevertheless, some drawbacks, such as, too expensive or too much sludge production and also heavy metals contamination, make them inappropriate to be use. Natural materials, with low cost, easily available, are becoming attractive as adsorbents materials (Kasak et al., 2015).

Therefore, this work investigates several materials, natural and commercial, with and without thermal treatment, that could act as phosphorus adsorbent agents. Thus, calcined waste eggshell (ES), commercial zeolites (USY and HY) and natural ground rock rich in calcium (M1), iron (M2) and aluminum (M3) were selected.

Experimental

Materials

Y zeolites (USY, ultrastabilized Y, CBV 500 and HY, CBV400) were obtained from Zeolyst International in powder form. Natural ground rock rich in calcium (M1), iron (M2) and aluminum (M3) were kindly supplied by CIMPOR as a powder. ES was prepared by egg shell calcination at $800^{\circ}\mathrm{C}$ during $2\ \mathrm{h}$. All chemicals used were of analytical grade. Deionised water was used for preparing solutions. HCl and NaOH solutions, $2.0\ \mathrm{M}$, were used as pH regulators.

Characterization analysis

The textural characterization was based on the N_2 adsorption isotherms, determined at $-196^{\circ}\mathrm{C}$ with a Quantachrome NOVA 4200 e apparatus. The samples were previously outgassed at $150^{\circ}\mathrm{C}$ under vacuum. The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated using the Boer t-method. Surface areas were calculated by applying the BET analysis (is the standard method for determining surface areas from nitrogen adsorption isotherms). The materials composition were analyzed by energy dispersive X-ray spectrometer (EDS). Absorbance measurements were made using a Shimadzu UV 2401PC UV-vis spectrophotometer.

Effect of pH

The effect of pH on phosphorus (P) removal by each adsorbent, was studied as described in Oliveira et al., (2012). The 0.1 g of ES was placed in contact with 50 mL solution containing $40 \mathrm{mgL}^{-1}$ of P , and 1 g of the other adsorbents with $1 \mathrm{mgL}^{-1}$ of P.

Kinetics of phosphorus removal

0.3 g of each material was placed in contact with 50 mL solution containing $100 \mathrm{mgL}^{-1}$ of P for ES and $1 \mathrm{mgL}^{-1}$ of P for all the other adsorbents. Initial pH was adjusted, 5 for ES, M1 and M2 and 7 for HY, USY and M3. Tests were performed in triplicate, at 200 rpm and $22^{\circ} \mathrm{C}$, for 2.5 h for ES and 5 days for the remaining adsorbents. The stirring was interrupted shortly at predetermined time intervals to remove solution to quantify the P concentration in the decanted and filtered supernatant solution. For ES, the concentration of P was measured at 10 min intervals during the first 30 min , then at longer time intervals. Regarding the remaining adsorbents, the concentration of phosphate was measured everyday. The amounts of P adsorbed by the different materials were calculated according to Eq. (1):

$$q=\left(C_{\mathrm{o}}-C_{\mathrm{t}}\right) \times \frac{V}{m} \tag{1}$$

where $q\left(\mathrm{mgg}^{-1}\right)$ is the mass of $\mathrm{P}(\mathrm{mg})$ removed per mass of material $(g), \mathrm{C}_{0}$ is the initial concentration of $\mathrm{P}\left(\mathrm{mgL}^{-1}\right), \mathrm{C}_{\mathrm{t}}$ is the concentration of $\mathrm{P}\left(\mathrm{mgL}^{-1}\right)$ at each time, V is the solution volume (L), and m is the mass of material (g).

Adsorption kinetics were preformed to determine the evolution of P uptake with time for all materials and analyzed according describe by Köse and Kıvanç (2011). Pseudo-first order and pseudo-second order models were applied to the experimental data to assess if the adsorption processes are controlled mechanisms.

Langmuir and Freundlich isothermal models were also applied to experimental data. From Langmuir equation, Webber and Chakkravorti established the separation factor $\left(R_{\mathrm{L}}\right)$, dimensionless constant that indicates the adsorption nature, unfavorable ($R_{\mathrm{L}}>1$), linear ($R_{\mathrm{L}}=1$), favorable ($0<R_{\mathrm{L}}<1$) or irreversible ($R_{\mathrm{L}}=0$) (Weber and Chakravorti, 1974) respectively.

Phosphorus adsorption isotherm

The extent of P adsorption from solution was studied using a batch contacting method. Adsorbents were weighed in a range of $20-700 \mathrm{mg}$. The materials were placed in a 50 mL solution containing $200 \mathrm{mgL}^{-1}$ of P for ES and $5 \mathrm{mgL}^{-1}$ of P for other adsorbents, respectively. The initial pHs were adjusted, ES, M1 and M2-5 and HY, USY and M3-7. Adsorption took place in sealed plastic Erlenmeyer flasks clamped into an orbital shaker at 200 rpm and $22^{\circ} \mathrm{C}$, during 72 h . The tests were performed in triplicate. At equilibrium, the P concentration in solution was measured as described in Oliveira et al. (2012).

Wastewater treatment

ES was selected to study the extension of P adsorption from wastewater inlet sample collected in a municipal wastewater treatment plant (WWTP). Batch contacting method was used, where 0.01 g of ES contacted with 50 mL of wastewater sample in sealed plastic Erlenmeyer flasks clamped into an orbital shaker at 200 rpm and 22°C, until equilibrium be reach. The average of wastewater pH was 6.9 with an initial P concentration of $5.9 \mathrm{mgL}^{-1}$.

Results and discussion

Materials characterization

The nitrogen adsorption-desorption equilibrium isotherms at $-196^{\circ}\mathrm{C}$ for both zeolites are of Type-I, according to the IUPAC classification, which is typical of solids with a microporous structure (Neves et al., 2010). The natural materials (ES, M1, M2 and M3) are of Type-II, caracteristic of non microporous materials with N_2 adsorption occurring in multilayers on the mesopores (Table 1). Among the natural materials, the BET surface area has the lowest value for ES ($4 \mathrm{~m}^2 \mathrm{~g}^{-1}$) and presents the following trend for the crushed minerals: M3 > M2>M1. Internal surface area and pore volume influence the adsorptive capacity of the adsorbents.

Both zeolites HY and ultrastable Y are faujasite structure with similar Si/Al ratio. Also, the minerals show similar chemical composition with M1 rich in calcium follow by M3 and M2 rich in aluminum and iron. ES, after thermal treatment, is mainly composed by calcium and oxygen.

Phosphosrus removal performance

The effect of pH on P removal capacity by the several sorbents is shown in Fig. 1. P uptake for ES and M2 was independent of pH values, for all pH range. However, pH seems to be an important parameter for the remaining materials. Zeolites (USY and HY) were

Table 1
Physical properties and chemical composition of the adsorbent materials.

Material	Porosity				Chemical composition (%)				
	S_{BET} (m^2 g	V_{micro} (cm^3	V_{meso} (cm^3	V_{T}(cm^3 g	Si	Al	Fe	Ca	Mg
ES	4	0	0.013	0.013	-	-	-	49.15	0.47
HY	665	0.302	0.047	0.349	34.2	11.7	-	-	-
USY	750	0.269	0.086	0.355	34.1	10.9	-	-	-

M1	16	0	0.034	0.034	12.23	3.03	1.48	43.21	1.76
M2	30	0	0.053	0.053	16.24	4.96	13.43	33.31	2.15
M3	38	0	0.063	0.063	18.47	5.98	3.02	35.17	2.75

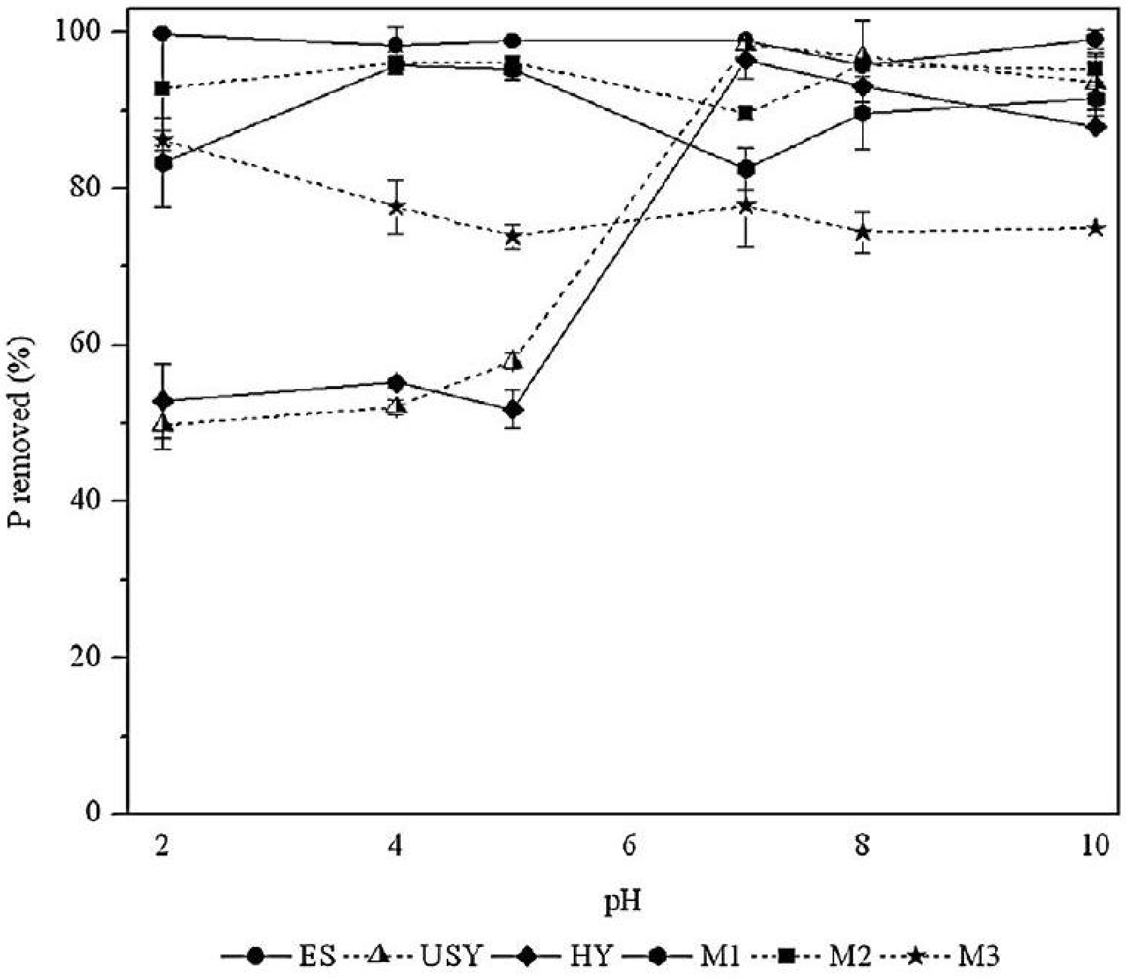

Fig. 1. Effect of pH on P adsorption by several sorbents materials. effective as adsorbents only in basic pH region (approximately $90 - 100\%$ uptake to pH ≥ 7). M3 (rock rich in aluminum) adsorption decreases as the pH increases, due to the aluminum intermediate formed and its solubility. M1 (calcium rich) shows similar behavior to M2, but with lower P removal performance. Data clearly

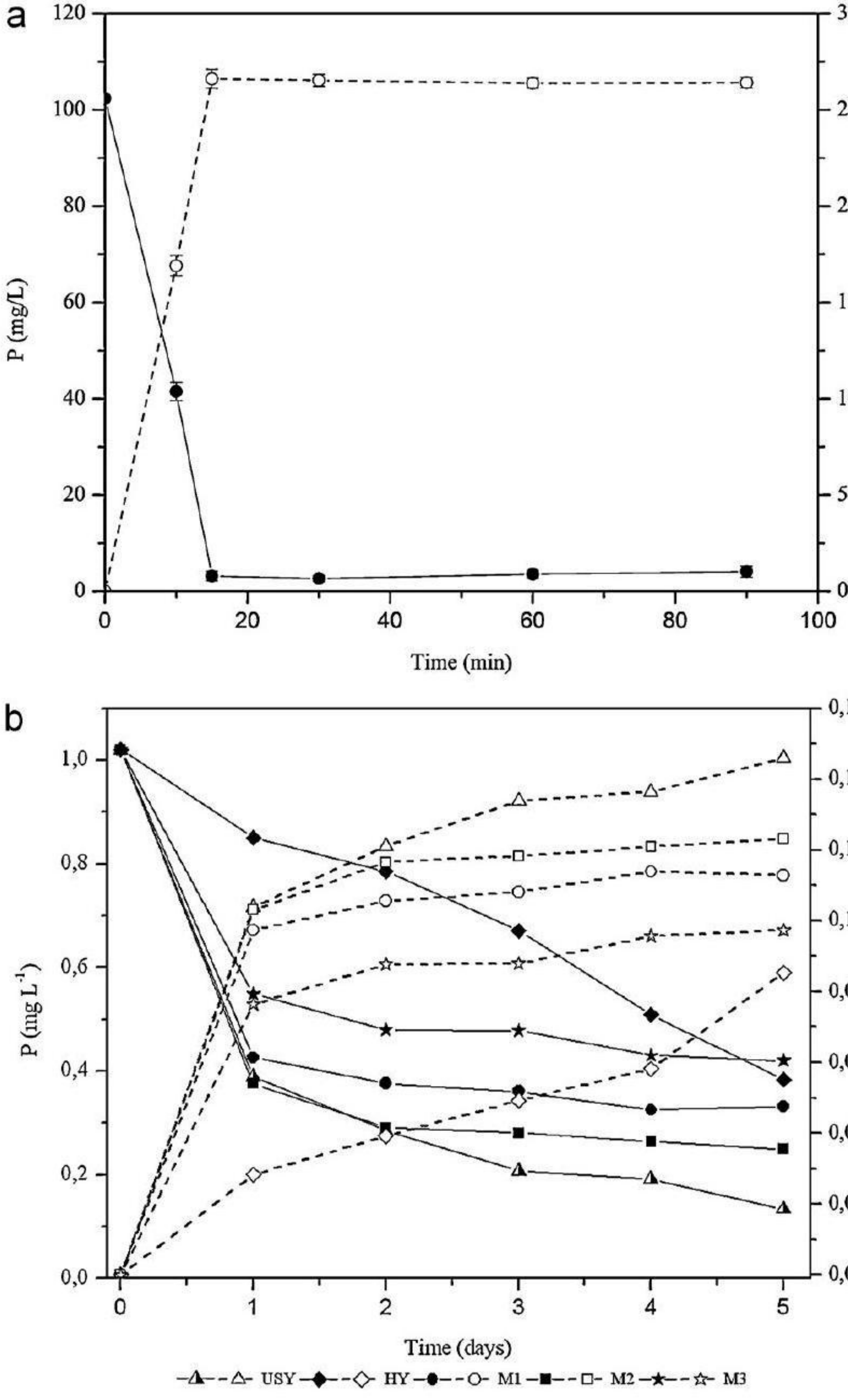
a
120
100
80
60
40
20
0
P (mg/L)
30
25
20
15
10
5
0
q (mg/g)
0
20
40
60
80
100
Time (min)
b
1,0
0,8
0,6
0,4
0,2
0,0
P (mg L-1)
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
q (mg g-1)
0
1
2
3
4
5
Time (days)
USY
HY
M1
M2
M3

Fig. 2. Kinetics of P adsorption (a) by ES , (b) by USY, HY, M1, M2 and M3. demonstrates that pH is a critical parameter in the adsorption process.

Fig. 2 presents the P adsorption results, which indicate that adsorption was time dependent for all materials. ES exhibited the faster P uptake, after $15 \mathrm{~min}, 98\% \mathrm{P}$ was already removed, remaining constantly after that. The remaining adsorbents, revealed a much slower P removal efficiency. With the exception of HY, P removal occurred predominantly in the first 24 h of contact, exhibiting the affinity between adsorbent and P species. After 4 days, P uptake remained almost constant for M1, M2 and M3. Zeolites, due to its microporous structure, depicted a continuous and gradual P uptake, requiring a longer equilibrium time to allow the diffusion of P through the microporous structure.

The P adsorption uptakes for the several adsorbents (q_{exp}) were determined and depicted in Table 2. Contrarily to what was expected from BET results (Table 1), larger specific surface has better adsorptive performance, ES showed the higher q_{exp} . Ionic permutation phenomenon could be a possible explanation for P uptake by ES. The remaining adsorbents, among them, indicated similar adsorption capacities.

The correlation coefficients, R^2, of pseudo-second kinetic model were higher in all cases (close to 1) than pseudo-first order. Moreover, $q_{\mathrm{e, cal}}$ are similar to experimental values. This indicates that pseudo-second model can describe the adsorption kinetics of P by different materials. Similar results have been reported by other authors (Köse and Kıvanç, 2011).

The interactive behavior between solute and adsorbents were studied by isothermal equilibrium to the different materials (data not shown). Adsorbents surface material saturation linearly decreases with an increase of its amount. This indicates that adsorption capacity depends on the amount of P transported from solution to the adsorbent surface and not on the amount of adsorption material presented. Material amounts around 0.7 g had sufficient adsorption sites to adsorb all P in the range of the studied concentrations.

Isothermal models provided accurate fits to the experimental data. However, Freundlich equation, except for M1, was the one that best fit to experimental data (higher R^2). The applicability of two isotherm models indicates that both monolayer adsorption and heterogeneous surface conditions exist, revealing that P adsorption involves more than one mechanism. Adsorption nature, R_{L}, was favorable for almost all materials and irreversible to M1 and M3. Dubinin-Radushkevich isotherms regression coefficients are lower than the Langmuir and Freundlich values. The E values, obtained from DR model, between 8 and $16 \mathrm{~kJ} \mathrm{~mol}^{-1}$, indicate that adsorption occurs by chemical process and lower than $8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ suggest a physical adsorption (Demiral et al., 2008). According to the E values obtained, while zeolites (HY and USY) adsorbed P by a chemical process, all the remaining adsorbents follow a physical process. This is in agreement with the nature determined by Langmuir model.

Since ES seemed to be the most promising material for P removal, it was selected to treat a municipal wastewater. Fig. 3 illustrates the results of dynamic adsorption of P from a wastewater inlet onto ES without pH adjustment.

The adsorption on ES surface occurs rapidly in the first 3 h reaching 80% of P removal. After approximately 3 h , adsorption sites were saturated and equilibrium was reached.

The adsorption capacity under the conditions tested was 22.3mgg^{-1}, similar to the value obtained in the kinetic test, despite of the complexity of the wastewater used.

Conclusions

Several natural materials were tested as P adsorbents to wastewater treatment. ES, M1 (calcium), M2 (iron) and M3

Table 2
Kinetic parameters for the adsorption of P onto several study materials.

	q_{exp} (mgg^{-1})	First-order kinetic model			Second-order kinetic model		
		k_1($1\ \text{min}^{-1\text{a}}$ or $1\text{day}^{-1\ \text{b}}$)	$q_{\text{e,cal}}$ (mgg^{-1})	R^2	k_2($\text{gmg}^{-1}\ \text{min}^{-1\text{a}}$ or $\text{gmg}^{-1}\text{day}^{-1\ \text{b}}$)	$q_{\text{e,cal}}$ (mgg^{-1})	R^2
ES	26.48	0.057 [a]	18.72	0.997	0.025 [a]	26.81	0.998
HY	0.14	1.008 [b]	0.07	0.926	14.738 [b]	0.15	0.999
USY	0.14	0.942 [b]	0.10	0.985	10.106 [b]	0.16	0.997
M1	0.11	0.844 [b]	0.04	0.963	35.361 [b]	0.12	0.999
M2	0.12	0.881 [b]	0.04	0.964	32.227 [b]	0.13	0.999
M3	0.10	0.962 [b]	0.07	0.811	23.037 [b]	0.10	0.997

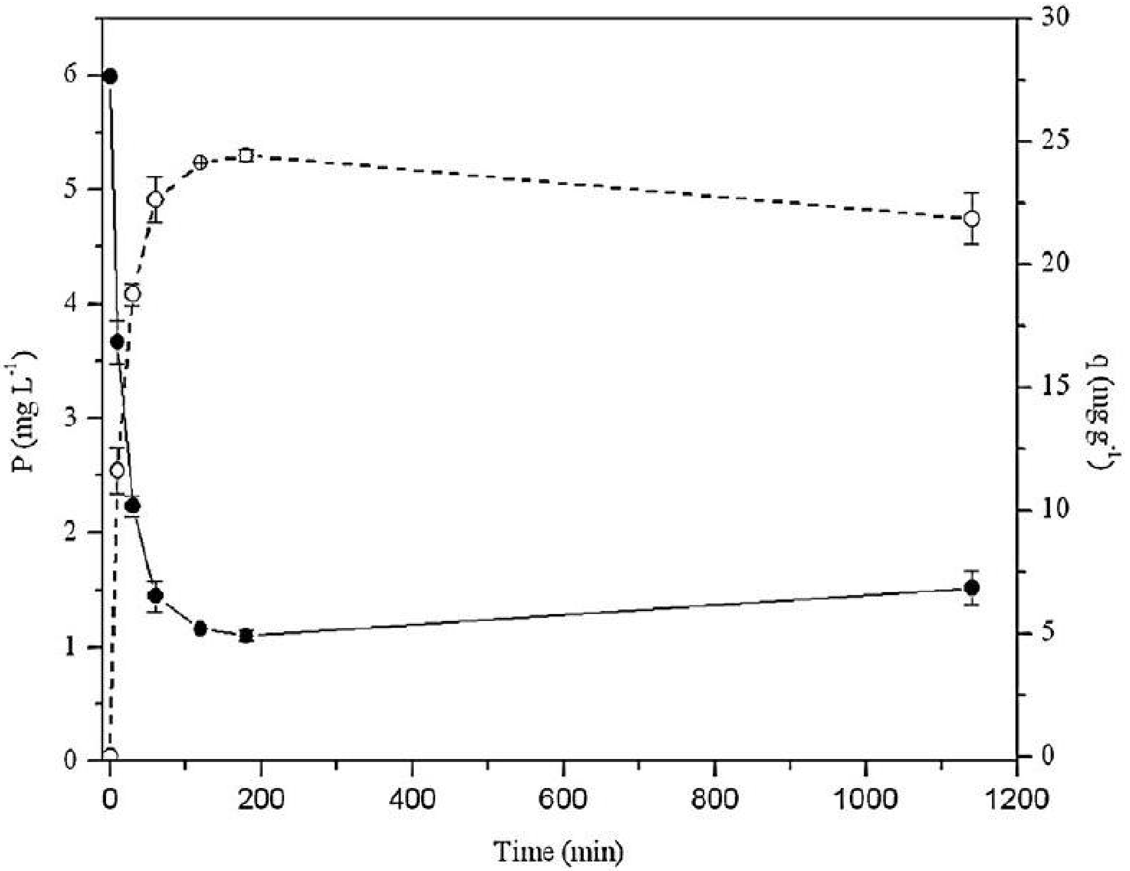

Fig. 3. Kinetic adsorption of P present in WWTP wastewater inlet onto ES. (aluminum) prove to be stable in the pH range from 2 to 10 , the zeolites (HY and USY) were pH sensible and exhibited higher adsorption at pH above 4.0. The kinetic data obtained with all materials fit very well to a pseudo-second order kinetic model. Langmuir and Freundlich equations described the adsorption data indicating that both monolayer adsorption and heterogeneous surface conditions coexist. With the exception of zeolites, the adsorption mechanisms were mainly physical. When ES was used to treat wastewater, its efficiency in P adsorption capacity was not significantly affected by the presence of other ions in complex wastewater.

Acknowledgments

The authors acknowledge the n-STeP - Nanostructured systems for Tailored Performance, with reference NORTE-07-0124-FEDER-

000039, supported by the Programa Operacional Regional do Norte (ON.2), PEst-C/CTM/LA0025/2013 and CIMPOR, Portugal.

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