



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



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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 0.10 mgP g⁻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.

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1. Introduction

All living organisms require essential nutrients, in particular phosphorus, for their growth, metabolism and reproduction (Pena-Pereira et al., 2011). Phosphorus, the 11th abundant element in crustal rocks of the earth, is predominantly found in the form of phosphate (PO₄³⁻) 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 used. 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.

2. Experimental

2.1. 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 °C during 2 h. All chemicals used were of analytical grade. Deionised water was used for preparing solutions. HCl and NaOH solutions, 2.0M, were used as pH regulators.

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2.2. Characterization analysis

The textural characterization was based on the N₂ adsorption isotherms, determined at –196 °C with a Quantachrome NOVA 4200e apparatus. The samples were previously outgassed at 150 °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.

2.3. 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 mg L⁻¹ of P, and 1 g of the other adsorbents with 1 mg L⁻¹ of P.

2.4. Kinetics of phosphorus removal

0.3 g of each material was placed in contact with 50 mL solution containing 100 mg L⁻¹ of P for ES and 1 mg L⁻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 °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):

$$q = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

where q (mg g⁻¹) is the mass of P (mg) removed per mass of material (g), C_0 is the initial concentration of P (mg L⁻¹), C_t is the concentration of P (mg L⁻¹) at each time, V is the solution volume (L), and m is the mass of material (g).

Adsorption kinetics were performed to determine the evolution of P uptake with time for all materials and analyzed according describe by Köse and Kivanç (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 Chakravorti established the separation factor (R_L), dimensionless constant that indicates the adsorption nature, unfavorable ($R_L > 1$),

linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Weber and Chakravorti, 1974) respectively.

2.5. 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 mg. The materials were placed in a 50 mL solution containing 200 mg L⁻¹ of P for ES and 5 mg L⁻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 °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).

2.6. 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 mg L⁻¹.

3. Results and discussion

3.1. Materials characterization

The nitrogen adsorption-desorption equilibrium isotherms at –196 °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, characteristic of non microporous materials with N₂ adsorption occurring in multilayers on the mesopores (Table 1). Among the natural materials, the BET surface area has the lowest value for ES (4 m² 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.

3.2. Phosphorus 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 ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	V_T (cm ³ g ⁻¹)	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

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