Effect of concrete carbonation on phosphate removal through adsorption process and its potential application as fertilizer

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Abstract

Concrete slurry is an abundant, cheap, and commonly found waste all over the world where construction activities take place; concrete slurry which is rich in calcium and metallic oxides could be successfully employed in the phosphate (P) removal from aqoueos media. In this research, the effect of the carbonation process over physicochemical properties and in the adsorption of phosphate on the concrete slurry powder was investigated.

The results showed that non-carbonated sample was more effective in the P removal due to higher releasing of Ca^{2+} in comparison to carbonated sample. The dissolved Ca^{2+} from the dissolution of $Ca(OH)_2$, $CaCO_3$, and CaO are preferably precipitated by phosphates in high pH solution, reflecting in a high initial adsorption rates.

General order kinetic and Liu isotherm provided the better fitting models for the adsorption behavior of P onto both non-carbonated and carbonated concrete samples. Phosphate removal was mainly ruled by chemical adsorption through inner-sphere complexation and P precipitation on the surface of the adsorbent containing Ca^{2+} as an essential element in the adsorption mechanism. Compared with other phosphate adsorbents, both non-carbonated and carbonated concrete may be an economical and efficient adsorbent.

The non-carbonated sample gave a high adsorption capacity of P (47.6 mg g^{-1}) and presenting fast and high initial adsorption, reaching 72% of P removal within 5 minutes (min) at 22°C, while carbonated showed adsorption capacity of 30.6 mg g^{-1}, at the same experimental conditions. Therefore, concrete slurries can be used widely as an inexpensive phosphate-recovery adsorbent.

Besides, the application of these loaded P waste, as potential fertilizers in soil can be an exciting and environmentally approach for reusing this solid-waste. The environmental analysis highlighted that the adsorbents did not leach out chemicals above the allowable limits preconized by FAO for irrigation waters. However, aspects

related to monitoring the presence and mobility of heavy metals on soil must be better addressed and monitored.

Keywords: Recycling slurry concrete; concrete-waste adsorbent; phosphate adsorption; potential fertilizer**.**

1. Introduction

Concrete is the most used popular material throughout the construction industry due to the several matters such as availability, accessibility, durability, and economic issues associated with its production and use (WBCSD 2019). However, with the rapid development of the industry of concrete fabrication all over the world, large quantities of by-products are produced (WBCSD 2019). The annual global concrete consumption reaches 25 billion tonnes. This production generates a large number of leftovers of fine powder slurry of concrete (Aynur and Ulubeyli, 2016). The leftovers are generated from Internal washing of the balloon of the concrete mixer truck and the washing process of the yard where the concrete blocks are placed.

Although it is difficult to determine precisely the waste volume generated, it is estimated that every day a concrete batching plant can generate about 0.4-0.5% of new concrete waste in the relation of its total production (Aynur and Ulubeyli, 2016). Therefore, it is imperative to explore the potential recycling of this type of fresh concrete, which the recovery and reuse of both fine aggregates and water can bring several benefits to the economic and environmental point of views (Aynur and Ulubeyli, 2016).

Over past few years, many types of reuse for slurry concrete have been proposed, such as concrete production itself (Bravo et al., 2018), mortar and ceramic materials (Cardoso et al., 2016), geopolymers synthesis (Vásquez et al., 2016), and others. However, there is also a high potential for using concrete slurries for environmental applications as eco-friendly materials. For instance, the concrete slurries

can be used as adsorbents for uptake pollutants in aqueous media by adsorption (Wang et al., 2014).

Adsorption is a widespread operation unit in which a specie named as adsorbate bound at the surface of the adsorbent. This process is a low-cost and effective technique for the removal of pollutants in aqueous media (dos Reis et al., 2016). An essential advantage of the adsorption process is that the adsorbents can be regenerated and reused many times, which makes the process even cheaper compared to others.

Sasaki *et al*., (2014) studied the removal of arsenate in aqueous solution, using concrete waste as adsorbents. The results showed high adsorption capacity and the primary adsorption mechanism was ion exchange between arsenic molecules and ions at the surface and matrix of concrete-waste adsorbents, in which ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) was at a higher amount. Littler *et al*., (2013) studied the adsorption properties of cement/concrete matrix in the removal of phosphate in aqueous solution. The results obtained appointed that during the adsorption process, cement/concrete matrix released Ca^{2+} in solution, which attracts and bind phosphate species, resulting in the precipitation reaction in the form of calcium phosphate solids. The same phenomenon was observed and related by Park *et al*., (2008).

Therefore, herein, it is proposed to evaluate the carbonation of slurry concrete and its influence on the slurry microstructure properties and how the carbonation process affects the adsorption of phosphate compounds in aqueous media.

Carbonation is a physical-chemical neutralization process as a result of the absorption of atmospheric CO_2 in the concrete pores, which reacts with calcium hydroxide ($Ca(OH)_2$) and other hydrated compounds of cement matrix to form calcite ($CaCO_3$) (Abass and Olajire 2013). Carbonation process can promote important changings on concrete surface microstructures, which can reflect in the adsorption properties.

The phosphates will be employed as adsorbate in this research. Indeed, phosphates are a vital nutrient that is essential for life. It is a crucial component added in

fertilizers for food production and has no substitute. Therefore, recovering phosphates from wastewaters are imperative (Sun et al., 2018). Phosphates in surface waters even at small concentrations can lead to the eutrophication, which poses a considerable risk to the ecosystem, resulting in environmental as well as economic damage (Sun et al., 2018). The presence of phosphates in natural waters comes from diffuse sources such as agricultural run-offs and municipal wastewater treatment plants (Ma et al., 2018). Hence there is a need for a method that can effectively dimish the phosphates to lower concentration or eliminate their presence in wastewaters before they are released in the environment.

Therefore, the overarching purpose of this study is to investigate the effect of progressive carbonation on microstructural and surface properties of the concrete slurry waste. Then, the presence of functional groups at the microstructure and pore structures of slurry before and after carbonation is also investigated. Lastly, the potential in the removal or recovery phosphates from aqueous solutions is tested.

2. Materials and methods

2.1. Raw material

The slurry concrete is generated from the washing of concrete mixer trucks and it is separated from wastewater as suspended solids at the ready-mixed concrete plants. The wet sample was collected from wastewater obtained during the washing of the concrete mixer truck ballons immediately after being discharged into the sedimentation tanks. Two buckets of fresh slurry concrete generated were collected (each one was about 30 kg of fresh slurry concrete).

A few hours later, the slurry of concrete became hardened, due to the hydration of residual cement. The dry material was then comminuted by a concrete mixer. After

136 homogenization and quartering processes, eight samples of about 100.0 g (passing the
137 1-mm sieve aperture) were obtained and named according to their ages as follows: 0, 7,
138 14, 21, 28, 35, 42, 49 and 56 days.

139 All the reagents were analytical grade and used as received without any further
140 purification. Potassium phosphate dibasic (K_2HPO_4) was purchased from Sigma-Aldrich
141 (DE). Deionized water was used for the preparation of the solutions, and ethanol was
142 procured from Beijing Chemical Reagents Company (China).

143

144 ***2.2. Accelerated carbonation process***

145

146 The dried slurry powder concrete (particle size < 1.00 mm) was placed onto
147 plastic disks and introduced in a carbonation chamber under the following conditions:
148 temperature of 23°C, CO_2 content of 5% and relative humidity of 65%. A total of eight
149 samples were conditioned for 8 weeks (56 days), and the effect of carbonation was
150 evaluated according to their ages, as shown in **Fig. 1**.

151

152

153 **Fig.1** Samples of slurry concrete numbered according to their ages.

154

155 ***2.3. Slurry concrete characterization***

The textural characterisation was carried out using N_2 adsorption-desorption isotherms at liquid N2, using a Tristar II Kr 3020 Micromeritics equipment. Prior analyses, the samples were degassed at 120 °C under vacuum. The specific surface area was determined by BET (Brunauer, Emmett and Teller) method (Umpierres et al., 2018).

The morphologies and majority elements of the concrete samples were observed with a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (TESCAN 3, Sweden) (Wamba et al., 2017).

The functional groups of the concrete slurry were determined using a Fourier Transform Infrared Spectroscopy (FTIR) with the ATR (Attenuated Total Reflectance) accessory, Bruker Spectrometer, alpha model (Thue et al., 2017).

Differential thermogravimetric (DTG) analysis was made by using a TA Instruments model SDT Q600 (New Castle, USA) with a heating rate of 10°C·min^{-1} at 100 mL·min^{-1} of the synthetic flow of air. The temperature was varied from 20° up to 1000°C (Wamba et al., 2017).

2.4. Adsorption tests

Several aliquots of 20.00 mL of phosphate solutions with diffrent initial concentrations ranging from 20.00 to 950.0 mg L^{-1} and at initial pH ranging from 2.0 to 12.0 were added into 50.0 mL Falcon tubes containing 0.03 – 0.5g (gram) of concrete-waste adsorbents. The flasks were capped and placed horizontally in a shaker, and the system was agitated between 5 min to 4 hours (h) (Leite et al., 2017). Afterward, the adsorbents were separated from the aqueous solutions by centrifugation using a Fanem centrifuge. Then the aliquots of 1–5 ml of the supernatant were properly diluted into 10.0–100.0 ml with a suitable blank solution (Leite et al., 2017).

The initial, as well as the residual phosphates concentrations, were quantified after adsorption experiments by using ICP-OES technique with Agilent 715 equipment. The content of phosphates adsorbed by the concrete-waste adsorbents and the

184 percentage of phosphates removed was calculated using Eq. 1, also, Eq. 2, respectively
185 (Kasperiski et al., 2018):

$$q=\frac{(C_o-C_f)}{m}.V \quad (1)$$

$$\%Removal=100.\frac{(C_o-C_f)}{C_o} \quad (2)$$

186 q is the quantity of P ions removed by the concrete absorbents in mg g-1 , Co is the initial
187 P initial concentration in the solution in mg L-1 , Cf is the P concentration after the batch
188 adsorption experiment in mg L-1 , m is the mass of concrete adsorbents in g and V is
189 the volume of P solutions in contact with the concrete adsorbents in L.
190
191 *2.4.1 Analytical control of the measurements and statistical evaluation*
192 See Supplementary Material and references (Leite et al., 2017: Kasperiski et al.,
193 2018).
194
195 *2.4.2. Kinetic of adsorption*
196
197 See Supplementary Material (Lima et al., 2015).
198
199 *2.4.3 Equilibrium of adsorption*
200
201 See Supplementary Material (Lima et al., 2015).
202
203 **3. Results and discussion**
204
205 ***3.1. The particle size distribution of the natural concrete used in the***
206 ***carbonation experiments***
207

Fig. 2 shows the particle-size distribution (PSD) of the fine fraction (ø < 1.00 mm) used for carbonation experiments. It is possible to see that the particle-size distribution analysis of the slurry concrete showed fine and continuous material containing 90% of particles lower than 56 µm (D_{90}) (See **Fig. 2**). Also, the slurry powder concrete presented D_{50} value (which is the particle size in which 50% of the total mass has passed through the sieve of ø < 1.00 mm) of 12.77 µm, and 10% of the material has a size of 2.37 µm. Smaller particles might have an influence on the carbonation process and even on the kinetic of adsorption and sorption capacity. This is because smaller particles have more surface area available to get in contact with the CO_2 (in the carbonation process) and also with the phosphate species during the adsorption experiments. Therefore, lower particles sizes can improve the adsorptive properties.

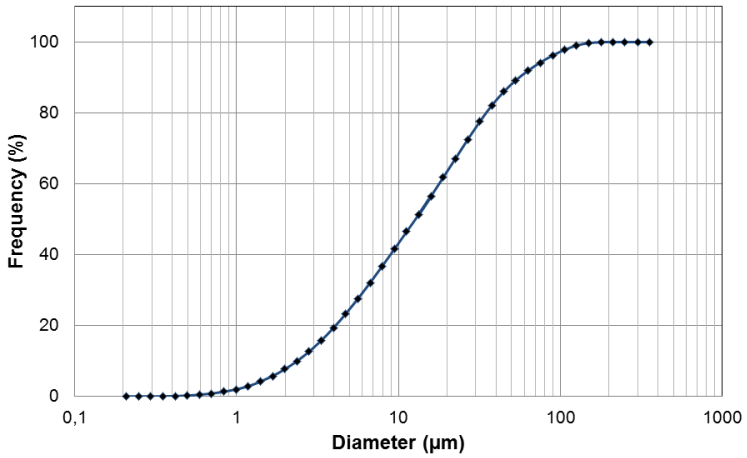


Fig. 2 - Grading curve of the concrete used for carbonation experiments.

3.2. Specific surface area and porosity

The values of the specific surface areas of slurries concrete samples before and after carbonation are presented in **Table 1**, that were obtained by nitrogen adsorption-

desorption isotherms. In general, the specific areas increased as the carbonation time also increased. These results justify that the crystallization of calcite minerals creates new porous surfaces during the carbonation process. In fact, during the carbonation process, the microstructure of concrete solid expands as the Ca^{2+} ions in the interlayer space progressively decreases due to the reaction between calcium ion and CO_2. This phenomenon will be further explained in section 3.3.

Insert table 1

Fig. 3 and Table 1 present the distributions of the pore sizes of the slurry samples, at different days of carbonation. The results show significant differences in the pore size diameter in two regions; around 10 nm and 90.0 nm. For the non-carbonated slurry (at zero-day) the incremental porosity was higher in the region around 90 – 100 nm. However, for the carbonated samples, the incremental porosity was higher in the region of 10 nm. Looking at Fig. 3A, it seems that as long as the carbonation is progressing the size of pores became smaller. This statement is strengthening by Fig. 3B, which shows that the cumulative porosity gradually reduced as carbonation progressed (Taylor 1978). These changes can have a decisive influence on the adsorption properties of both non-carbonated and carbonated samples.

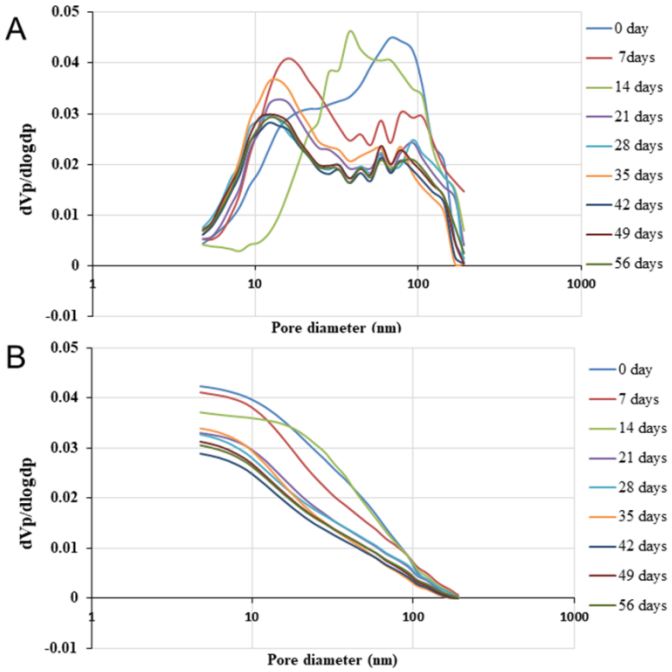


Fig. 3. The pore size distribution of carbonated concrete slurry

3.3. Surface features of the adsorbent samples

The surface morphology of the carbonated samples revealed by SEM might reinforce what was discussed in section 3.2. The SEM images are shown in the Fig.4. It shows that the surface of the carbonated slurry sample at the 7 days presented a smooth surface where no porosity can be observed. However, as long the carbonation is progressing the surfaces of the carbonated samples get more irregular and rougher (see Fig. 4), which may increase the porosity. This should be attributed to the formation and precipitation of the $CaCO_3$ (see red arrow in Fig.5) on the particle surface of slurry concrete due to the carbonation of the hydration products. As can be seen at 56 days of carbonation under given conditions, the surface of slurry concrete is almost totally covered by $CaCO_3$.

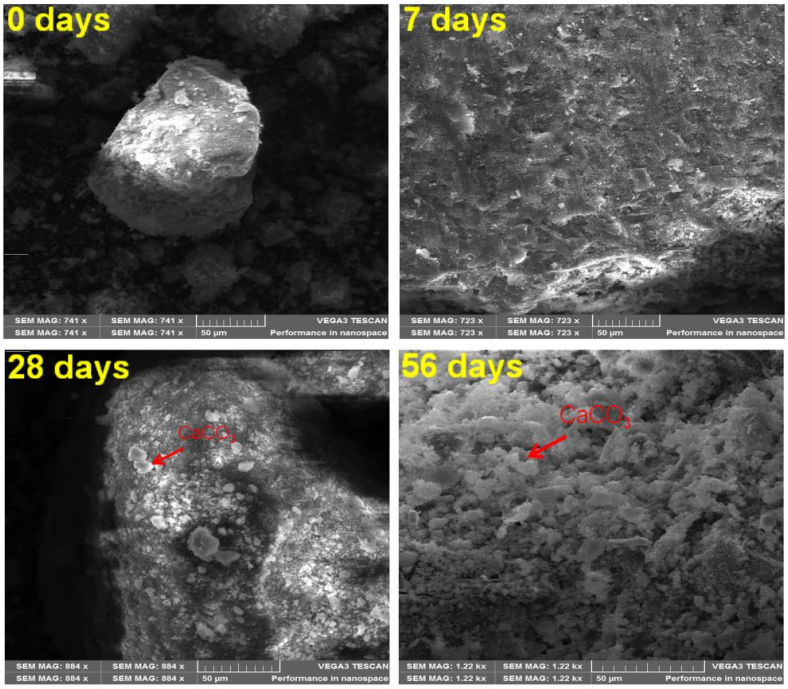


Fig. 4. Typical SEM images of the slurry samples at different ages of 0, 7, 28, and 56 days of the carbonation process.

Fourier transformation infrared spectroscopy (FTIR) can detect the presence of C–O in the concrete slurry to determine the presence of carbonate ($CaCO_3$). The spectrum of each slurry sample was determined by ATR, which allow determining the effect of the carbonation through the different ages. The FTIR spectra of non-carbonated and carbonated slurry concrete are shown in Fig. 5. As can be seen, all samples presented similar spectrums, and the main difference is in the intensity of the bands. It is possible to see in Fig. 5 that the bands get more intensive as the carbonation time increased, which might indicate that more carbonate is being formed. The major bands are listed as sulfate band in 1006 cm^{-1} (Wamba et al., 2017), anhydrous calcium silicates bands in 514 cm^{-1} while carbonate phases were in 1409, 871 and 774 cm^{-1} (Wamba et al., 2017).

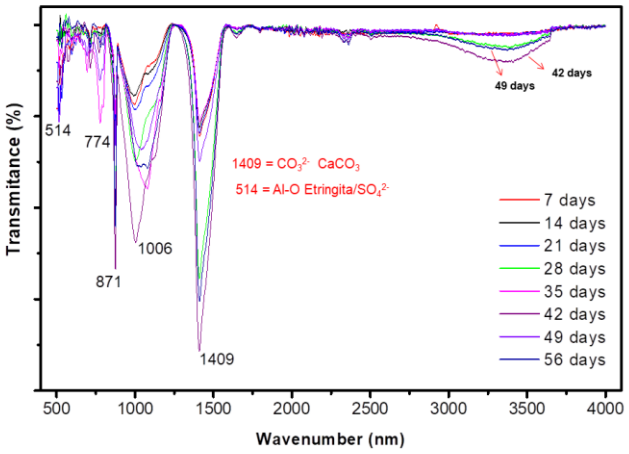


Fig. 5. FTIR spectrums of the carbonated slurry concrete samples.

The colorimetric test with phenolphthalein carried out for the sample at the 56 days of carbonation time, showed that the applied time process was enough to reach almost at the total carbonation of the concrete slurry was as it can be seen in supplementary **Fig. 1**. From the first days (natural concrete slurry) up to 28 days, the purple color shows that the carbonation process did take place under such selected conditions in this work. However, after 35 days (see supplementary Fig. 1) the carbonation seems to evolve until its process gets completed at 56 days. These observations can be better verified by using TGA-DTG and DRX analysis, what is shown in Section 3.4 (see Fig. 6).

3.4. Derivative thermogravimetric of the concrete samples

Derivative thermogravimetric (DTG) analysis has been used as a tool to study the carbonation reaction in concrete material. As we can see in Fig. 6, the first broad peaks between 74° and 106°C for both carbonated samples (28 and 56 days), and non-carbonated sample (0 days) referred to the moisture releases from samples. The second mass loss peak around 455°C correspond to calcium hydroxide dehydration, and it is

typical for the three samples (Tracz and Zdeb, 2019). However, for the non-carbonated sample, the peak was more intense, due to the higher content of $Ca(OH)_2$. The $Ca(OH)_2$ dehydration chemical reaction takes place, as shown in the following equation (Tracz and Zdeb, 2019):

$$Ca(OH)_2 \rightarrow CaO+H_2O \quad (3)$$

Finally, the peak at 710°C corresponds to the decomposition of the carbonates, where we can notice more intensive peaks in carbonated samples. A higher amount of $CaCO_3$ is expected in carbonated samples compared to the natural slurry concrete. Equation (4) shows the portlandite carbonation reaction, while equation (5) shows the de-carbonation equation (Tracz and Zdeb, 2019).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3+H_2O \text{ (carbonation)} \quad (4)$$

$$CaCO_3 \rightarrow CaO+ CO_2 \text{ (de-carbonation)} \quad (5)$$

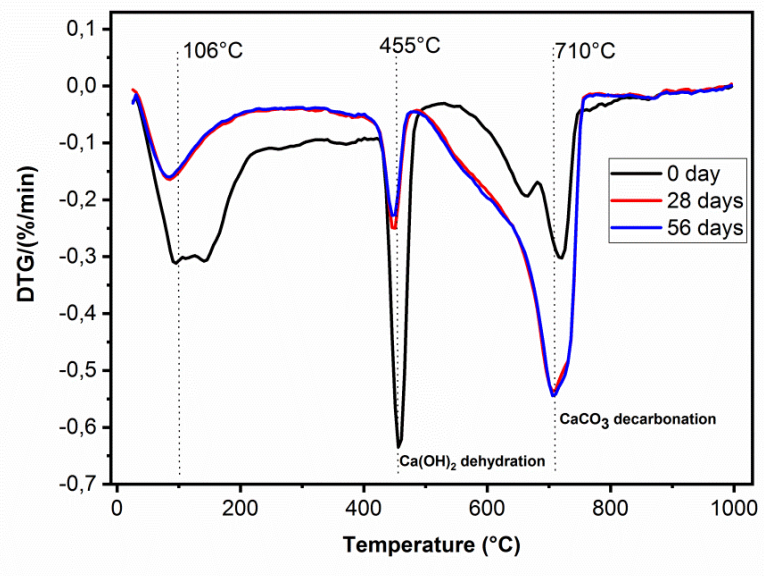


Fig. 6 - DTG curves for 0, 28 and 56 days of carbonation

3.5 Adsorption studies

3.5.1 Effect of Adsorbent Mass

318

319 The adsorbent dosage in the adsorption step is a crucial factor in making the
320 adsorption process applicable in real industrial scale.

321 **Fig. 7** describes the effect of mass concrete adsorbent (ranging from 0.0300 to
322 0.5000 g) on P removal using non-carbonated concrete. For the adsorption tests, a fixed
323 volume of 20.0 mL of P solution at an initial concentration of 240.0 mg L^{-1} was used. **Fig.**
324 **7** shows that the P sorption percentage increases, from 40 to 100%, as the adsorbent
325 dosage increases, from 0.0300 to 0.1500 g, respectively. Adsorbent masses beyond
326 0.1500 g keep the percentage removal constant while the amounts of adsorbed P per
327 unit weight (q_e) of the concrete-waste adsorbent decreased when increasing the mass
328 of solid/volume of solution ratio (see **Fig. 7**).

329 The rapid increase of the P adsorption as the adsorbent dosage increases
330 indicates the accessibility of a more significant number of sorption sites at a higher
331 dosage to adsorb P ions (see **Fig. 7**). This result suggests that high numbers of free
332 adsorption sites were available during the first stage of the process and then, as time
333 passes, the free remaining sites were less and became more difficult to be occupied due
334 to repulsive forces between the adsorbate and adsorbent particles (Choi et al., 2016).

335 The most effective adsorption result for phosphate was attained at 0.1000 g with
336 84.3% of P removal meaning a "q_e" of 41.3 mg·g^{-1} while 0.1500 g reached almost 99.2%
337 but with a "q_e" of 32.6 mg·g^{-1} (see **Fig. 7**). The choice of the mass of 0.1000 g to be
338 considered the most efficacious lies in the fact that 0.1500 g is 50% higher, compared to
339 0.1000 g, and achieves adsorption capacity only 15% higher. Also, the "q_e" for the 0.1g
340 is 21.1% higher than 0.15g.

341 Therefore, for further experimental studies, the adsorbent dosage is optimized at
342 0.1000 g in 20.0 mL of solution (5.00 g L^{-1}). Based on the above observations, it becomes
343 evident that phosphate adsorption is majority a phenomenon of the surface. Indeed the
344 amount of surface vacant sites for adsorption and therefore the mass of adsorbent can
345 extensively influence adsorption efficiency.

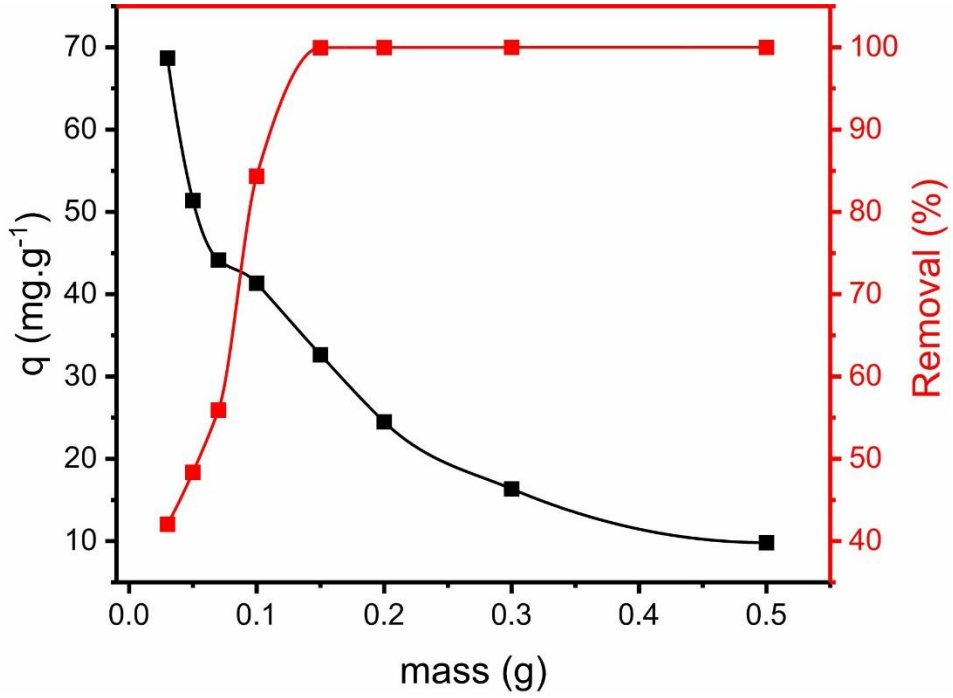


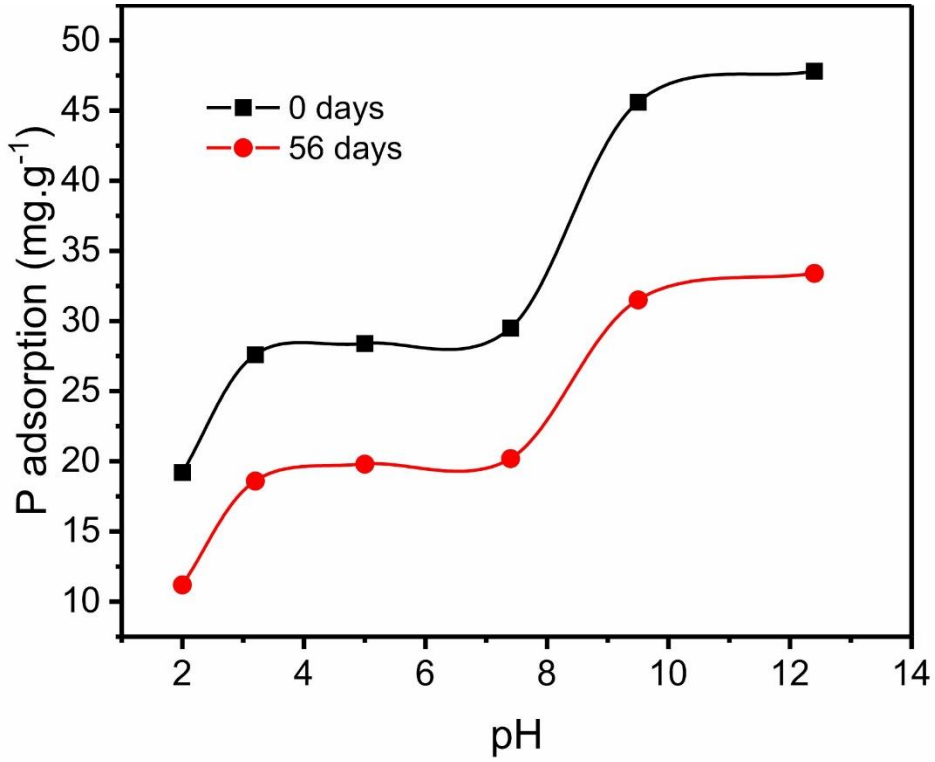
Fig. 7. Effect of adsorbent dosage on P removal using non-carbonated sample (0 days).

3.2.2 Effect of the pH on P removal

Changes in pH may affect the adsorption process either dissociating the adsorbate in different species and functional groups present at the adsorbent's active sites. Thus, it is necessary to know the influence that this parameter has on the process of adsorption of phosphate in aqueous solution.

Depending on the pH on the P solution, many phosphates species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) can be present at different proportions (Xie et al., 2014). **Fig. 8** shows the influence of pH on P removal by both samples (0 and 56 days of carbonation). The results show that at pH 2.0 "*q*" was the lowest for both adsorbents. For the non-carbonated sample (0 days), while the pH increases from 2.0 to 3.2 the "*q*" increased 30% and kept almost constant until pH 7.4 (29.5 $mg.g^{-1}$) (see **Fig. 8**). However,

364 when the pH increases from 7.4 to 9.5, the "*q*" increased by 35% (45.6 $mg.g^{-1}$). At pH
365 12.4, the adsorption capacity increases slightly and reaches 47.8 $mg.g^{-1}$. The same trend
366 was observed for the carbonated sample at 56 days; however, with less efficiency (see
367 **Fig. 8**).



368

369 **Fig. 8 -** Effect of the pH on P removal using non-carbonated (0 days) and
370 carbonated samples (56 days).

371

372 The reason for which each pH has different "qe" value can be explained due to P
373 adsorption could be influenced by the presence of Ca^{2+} dissolved ions (that is one of the
374 majority element in concrete waste). Calcium(II) ions can react with the phosphate
375 species present in the solution to form the solid calcium phosphate (Yuan et al., 2015).
376 As was aforementioned, the presence of the phosphate species mainly depends on the
377 solution pH values (Yuan et al., 2015). When pH value is about 9.5, HPO_4^{2-} is the
378 dominant specie in the solution (Yuan et al., 2015). Yan *et al*. (2007) pointed out that at
379 higher pH values, calcium phosphate precipitation is the primary mechanism for P
380 removal from aqueous solution.

The literature describes that the concentration of dissolved Ca^{2+} decreases when the pH initial value increases and this provokes the inhibition of calcium phosphate precipitation and then reduces phosphate adsorption (Yan *et al*. 2007; Yuan et al., 2015). This behavior was observed in this work for both non-carbonated and carbonated samples (see **Table. 2**).

Insert Table 2

Based on these results, it can be pointed out that, at higher pH values, calcium phosphate precipitation is one of the most predominant mechanisms in P removal from aqueous solution by using concrete-waste adsorbent. It is reported that P adsorption is hindered in alkaline environment because of the competition for surface active sites by hydroxide and phosphate ions (Johansson and Gustafsson, 2000). The acid pH helps the concrete body to release Ca^{2+} ions into the solution which react with the P causing the precipitation of $Ca_3(PO_4)_2$ (Yan *et al*. 2007). The enhance in P removal above pH 7.8 could be due to the formation of OH enriched complexes precipitating calcium phosphate (Yan *et al*. 2007).

3.2.3 Effect of the temperature on P removal

P removal onto concrete-waste adsorbents was also studied as a function of temperature. Results obtained in this study are given in **Fig. 9**. As shown in **Fig. 9**, the adsorption capacity increased as the temperature increased, and that the adsorption of P by the concrete-waste adsorbents most likely occurs through chemical interactions rather than physical interactions.

Fig. 9 shows that at 22°C, the P adsorption was 18.1 and 29.5 mg g^{-1} for carbonated and non-carbonated samples, respectively. When the temperature increase from 22° to 50°C the adsorption capacities increased to 26.1 and 38.4 mg g^{-1} for

carbonated and non-carbonated samples, respectively, corresponding to an increase in the order of 44% and 30% for both carbonated and non-carbonated samples, respectively. These results agree with early report (Li et al., 2016).

Although the temperature is an essential parameter in the P adsorption over concrete samples, the increase in the temperature results in a very high operational cost for the adsorption process, therefore, 22°C was selected as an optimum temperature for the kinetic and equilibrium experiments.

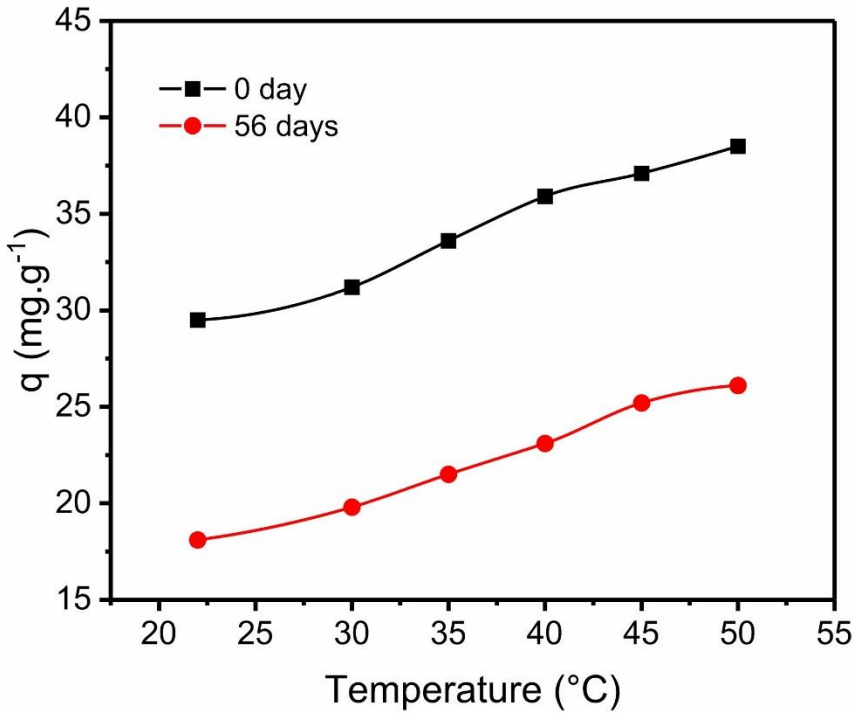


Fig. 9 - Effect of the temperature on P removal using non-carbonated (0 days) and carbonated samples (56 days).

3.2.4 Kinetic study of the adsorption

Kinetic adsorption process gives insights about the interaction between the used adsorbent and adsorbate and its importance in the process to obtain the equilibrium.

P ions adsorption on both concrete-waste adsorbents were very fast at the beginning of the process and reached 50% of P removal in 2.19 and 5.79 min for 0-day

427 and 56-day adsorbents, respectively; afterward, the P was slowly adsorbed achieving
428 95% of removal in 71.54 and 103.7 min for non-carbonated (0-day) and carbonated (56-
429 days) adsorbents, respectively.

430 Adsorption of P on both samples can be split into three stages:

431 (i) the rapid adsorption at the beginning of the kinetic, due to many available
432 active sites that easily adsorb P ion species on the surface of the concrete
433 adsorbents;

434 (ii) the slow adsorption in the second stage which suggests that the active sites
435 are becoming saturated;

436 (iii) The equilibrium characterized by a plateau, which corresponds to the
437 saturation of the adsorbent sites.

438

439 It is worth to note that in the calcium-rich adsorbents such as concrete, phosphate
440 is also precipitated and can be removed by an ion-exchange mechanism between
441 calcium species present at the surface of the adsorbents and phosphate species in
442 solution, rather than a fixation at the surface of the adsorbents as commonly found in the
443 literature (Rahnemaie and Hiemstra, 2006; Sabah and Majdan, 2009; Kudeyarova,
444 2010). Therefore, the adsorption mechanism in this study is different from that of
445 conventional adsorbents listed in the literature, such as activated carbons. The dissolved
446 Ca^{2+} from the dissolution of $CaCO_3$, CaO and $Ca(OH)_2$ are preferably precipitated by P
447 species (in phosphate form) in high pH solution, which gives a high initial rate of sorption.

448 Therefore, the adsorption of P onto concrete-waste adsorbents probably resulting
449 from a significant presence of many functional groups and oxides that are effectively
450 involved in the P capture as well as ion exchange mechanisms (Choi et al., 2016).

451 The fitting curves were analyzed by three models, pseudo-first-order, pseudo-
452 second-order, and general order kinetic model. The fitting curves and their parameters
453 are exhibited in **Fig. 10** and **Table 3**. It appears that the kinetic data is more suitable to
454 characterize the General order model.

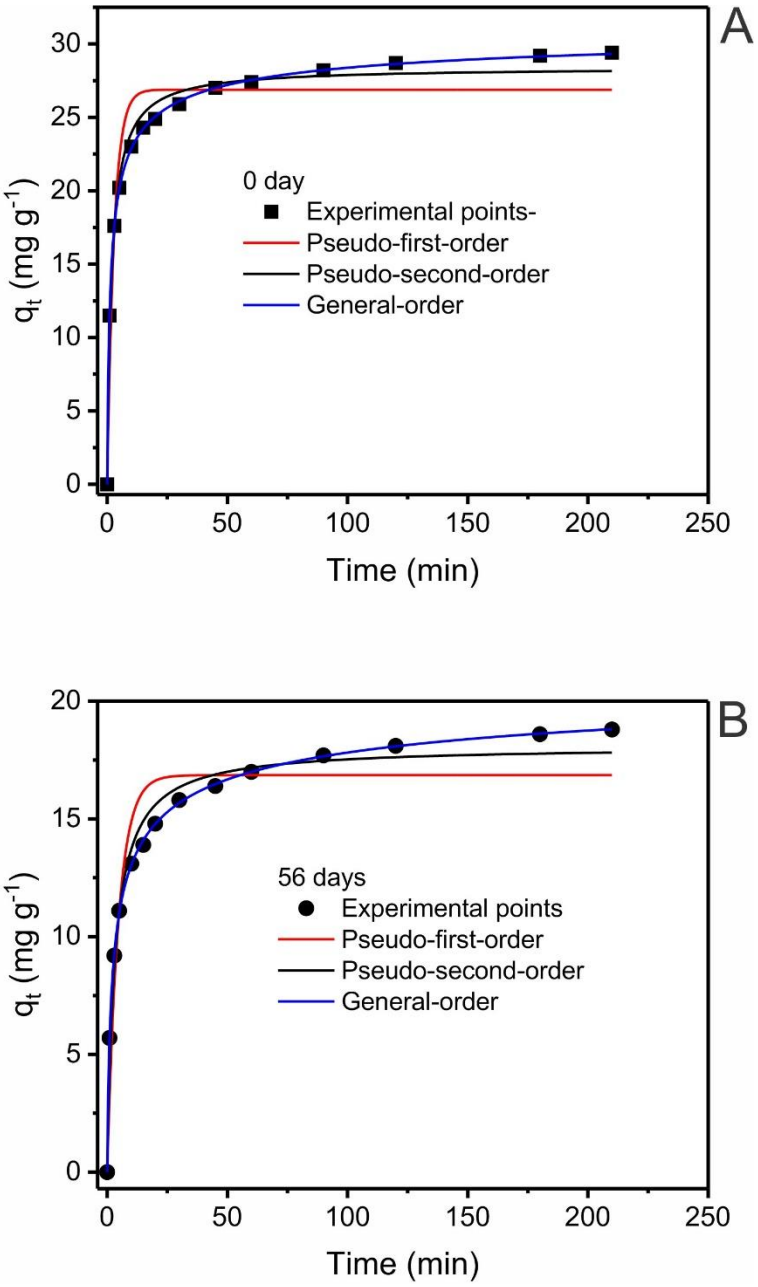


Fig. 10 - Kinetic curves for adsorption of P (A) non-carbonated and (B) carbonated samples.

Insert Table 3

The fitness of the kinetic models was evaluated according to the adjusted determination coefficient (R^2_{adj}), and standard deviation of residues (SD). Lower SD and higher R^2_{adj} values imply a smaller difference between experimental and theoretical *q*

values (which is given by the models) and therefore have the best suitable model. According to **Fig. 10** and **Table 3**, the general order kinetic model was the most suitable (for both adsorbents) model which best represent the experimental kinetic data, since they presented lower SD (0.1203 and 0.09344) and higher R^2_{adj} values (0.9998 and 0.9997), for both 0-day and 56-day adsorbents, respectively (see **Table 3**). This indicates that the q_t predicted by the General order model presented the closest calculated values compared to the experimental qt.

The general order kinetics describes that the order of adsorption should be the same as that of a chemical reaction which makes more sense in P removal onto concrete-waste adsorbents. It is well-known that P species (phosphate anions) are chemisorbed on the surface of metal-containing soil sorbents with the formation of hardly soluble metal–phosphate complexes (Rahnemaie et al., 2006; Kudeyarova, 2010).

3.2.5 *Equilibrium models*

The determination of the adsorption isotherm presents an indispensable role in the design of both methods fixed bed and batch adsorptions, besides allows to a better understanding of the whole adsorption process.

There are several isotherm models to evaluate equilibrium studies. In this research, Langmuir, Freundlich, and Liu isotherms were chosen to evaluate the fitness of the P adsorption over two concrete-waste adsorbents, a non-carbonated sample and carbonated one. The aim is to evaluate how the carbonation process affected P maximum adsorption capacity.

The P adsorption isotherm curves and their parameters for the adsorbents at 0 and 56 days of carbonation are displayed in **Fig. 11** and **Table 4**. The fitness of the models was evaluated using the R^2_{Adj}, and *SD* similar to the kinetic studies discussed above.

In the light of R^2_{Adj} and *SD* values, the equilibrium adsorption is more suitable to be described with Liu model, because it has the highest R^2_{adj} and the lowest *SD* values, in comparison with Langmuir and Freundlich models. This finding means that Langmuir and Liu's isotherms show lower goodness of fit, which means that these models do not describe well the adsorption process of P for concrete adsorbent used in this work under applied conditions. Likewise, the *q* values provided by the Liu model were closer to those obtained experimentally.

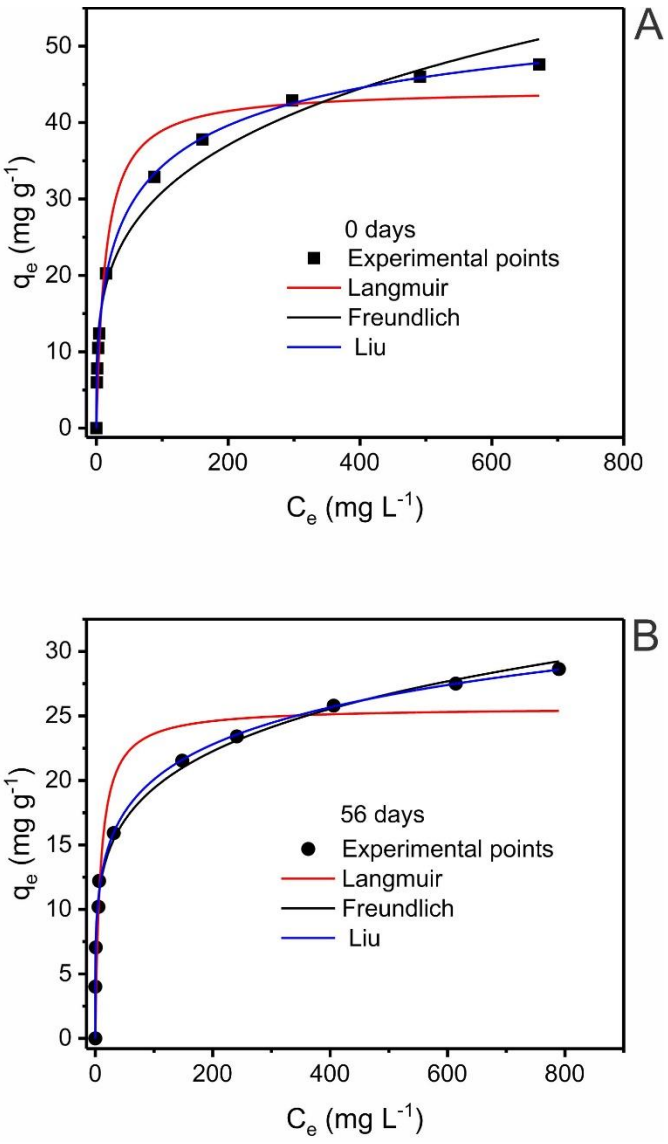


Fig. 11 – Adsorption isotherm curves of P for (A) 0 day and (B) 56 days.

Insert Table 4

3.2.5 *Adsorbent efficiency*

The evaluation of the effectiveness of the adsorption process depends on the adsorbent efficiency in terms of how it can uptake the desired pollutant. The adsorbent efficiency is usually performed from the comparison of the values of maximum adsorption capacities. To make a comparison among the results found in this paper, supplemetary **Table 1** summarizes the adsorption capacities and the main conditions and conclusions of some concrete/cementitious adsorbent materials in P removal from aqueous media in the literature.

The non-carbonated and carbonated samples (0 and 56 days, respectively) exhibited Q_{max} values of 63.85 and 63.83 mg g^{-1} (obtained from Liu isotherm model) which are among the highest adsorption capacities of that of other low-cost adsorbents cited in the literature (see supplemetary **Table 1**).

The reasons for different Q_{max} values for P adsorption might be justified by the fact that these works have used different experimental conditions such as different adsorbents, contact time, pH, and different isotherm models used (Langmuir, Liu, etc.). supplemetary **Table 1** also highlights from different experimental conditions ones can be obtained different findings and conclusions.

However, it is possible to infer that, based on supplemetary **Table 1**, the adsorbents used in this paper presented pretty good effectiveness for P adsorption and recovery from aqueous effluents since it is abundant and cheap to be enabled for adsorption experiments.

3.2.6 Possible mechanisms of phosphate removal

530

531 The adsorption of P species ions on the negatively-charged surface of concretes
532 and the precipitation of phosphate compounds can both respond for the majority of P
533 removal and recovery. Additionally, electrostatic interactions might also take place in the
534 mechanism of P adsorption on concrete. The importance of each adsorption mechanism
535 is probably determined by the pH of the adsorbate solution (Choi et al., 2016; Tracz et
536 al., 2019).

537 Before adsorption tests, the initial pH values of P solutions were around 7.6.
538 However, after adsorption tests, the pH was always higher than 10.0; this indicates that
539 the surfaces of both adsorbents were negatively charged.

540 Under very acid solution, the concrete surface is positively charged, which favors
541 the uptake of negatively charged phosphate ions due to the adsorption reactions and the
542 electrostatic attraction.

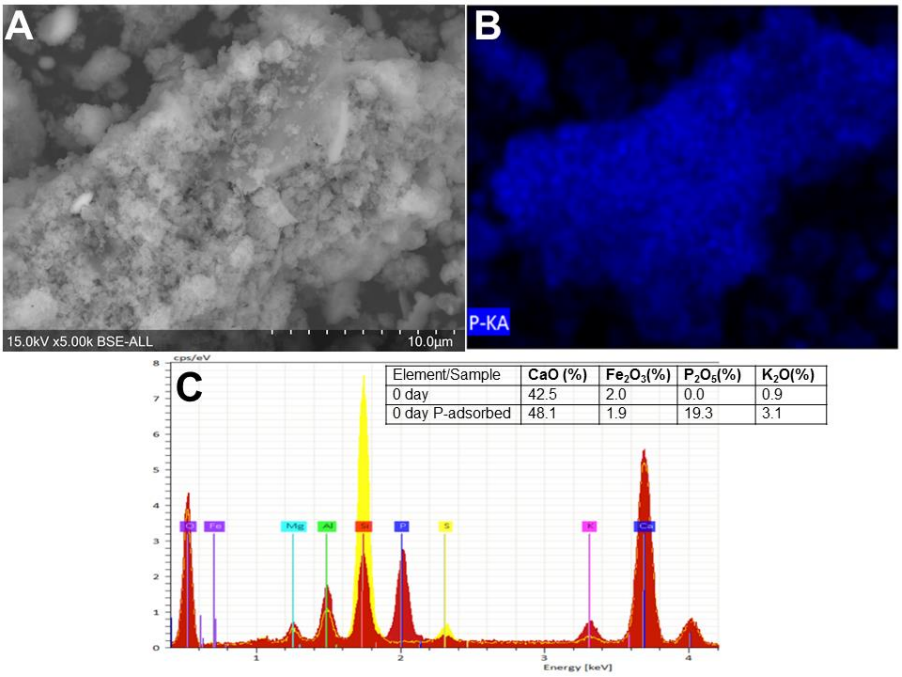
543 In the surface complexation mechanism, the adsorption of phosphate takes
544 place, on concrete surface, when part of hydroxyl groups on its surface from different
545 oxides (e.g., Fe—O--H, Ca--O—H…, etc) could be replaced by P anions and
546 subsequently the new Fe--O--P and Ca--O--P inner-sphere complexes could be formed
547 (Rahnemaie et al., 2006). Inner sphere complexes indicate that they are strongly bonded
548 to highly structure mineral surfaces and P via covalent binding (Rahnemaie et al., 2006;
549 Sabah and Majdan, 2009). The $H_2PO^-_4$ and HPO_4^{2-} can also react with some oxides (eg.,
550 Si--O--H, Ca--O--H, Al--O--H…etc) via hydrogen bonding according to follows (Sabah
551 and Majdan, 2009).

552 Deng and Wheatley (2018) reported the same findings concerning the P
553 adsorption mechanism on concrete-waste adsorbents. They showed that the P species
554 were mostly adsorbed due to the presence of the oxides of Ca, Al, Mg, and Fe, which
555 can effectively bind with P (e.g., phosphate) in aqueous solution.

556 Another mechanism of P removal in concrete - P solution system is the calcium
557 and metal oxides precipitation, being Ca^{2+} the major element that influence in the P

558 precipitation in the form of calcium-phosphate. Concrete-waste adsorbent leaches out
559 Ca^{2+}, and Ca^{2+} reacts with HPO_4^{2-} and PO_4^{3-} to form calcium phosphate. The same
560 precipitation mechanism might happen for other metals oxides such as Fe, Al, Mg, etc.

561 The **Fig. 12** shows the SEM and EDS mapping of the main elements found in
562 non-carbonated concrete loaded with phosphate. It shows that the main element is CaO
563 and the presence of P was detected in sample used in the P adsorption, highlighting that
564 non-carbonated sample successfully adsorbed the P.



Element/Sample	CaO (%)	Fe_2O_3(%)	P_2O_5(%)	K_2O(%)
0 day	42.5	2.0	0.0	0.9
0 day P-adsorbed	48.1	1.9	19.3	3.1

565

566 **Fig. 12** SEM and EDS mapping of the non-carbonated slurry concrete loaded P.

567

568 ***3.2.7 Environmental analysis (Leaching out tests) of concrete samples***

569

570 The leaching out method was used to investigate the leaching of trace elements
571 from the non-carbonated (0 days) and carbonated (56 days) concrete-waste adsorbent
572 used in this work and the target trace elements are presented in **Table 5**. The leached
573 out elements, even in tiny contents, can decrease the P removal efficiency due the
574 competition for adsorption. Moreover, the effect of coexisting elements (with different
575 concentrations) on P removal efficiency is a complex process, and it is difficult to

generalize on removal performance based only on laboratory scale experiments. Furthermore, the leaching of elements contained in the concrete adsorbents needs to be further investigated for the case of real polluted waters.

It can be seen that, despite the variability, all-metal levels released in the water from both concrete samples were within the allowable limits for agricultural soil irrigation purposes preconized by FAO (Ayers and Westcot 1985). Among all metals evaluated in **Table 5**, only the molybdenum exceeds the limit imposed by FAO (Ayers and Westcot 1985) in terms of waters used for irrigation. The rest of metals are below the limit which recommends maximum concentrations of trace elements in irrigation water. However, Ca and K seem to exceed the limits preconized by FAO (Ayers and Westcot 1985).

However, it does not represent a hazard because in this case, we are handling with wastewaters. Besides, for the leaching out tests were used a considerable amount of concrete (dosage of 30.0 $g.L^{-1}$) compared with those amounts used for the kinetic and equilibrium tests (dosage of 5.00 $g.L^{-1}$); therefore it is expected that the real valor would be lower than those presented in **Table 5**. In general, non-carbonated samples leached out higher element contents when compared to carbonated sample (see Table 5). The carbonation process improves the mechanical properties of the concrete-waste, which difficult the leaching elements out of the concrete matrix.

3.2.8 Viability and advantages of use P adsorbed on concrete as potential P-fertilizer

Cementitious waste come as promising materials for the designing of inexpensive phosphate adsorbents because they contain many oxides and alkali calcium compounds that are effective in phosphate capture and recovery.

The conventional processes employed today for P removal are chemical precipitation, ion exchange resins, biological activated sludge. These processes can achieve high efficient results for P removal; however, they present high costs and difficult

603 to be implemented. Adsorption process is easy to be implemented and is economically
604 viable.

605 Concrete-waste adsorbents have shown to have high P-removal performance
606 and therefore can be used as an inexpensive P recovery agent. Moreover, its natural
607 and environmentally friendly features make it suitable to be used as a fertilizer or soil
608 conditioner such to correct soil acidity. Concrete contains many essential macronutrients
609 (P, K, Ca, Mg), micronutrients (Fe, Mn and B) and some beneficial elements (Si, Na) for
610 plant growth and therefore it is useful for agricultural purposes.

611 Besides, the use of P-loaded adsorbent as a fertilizer could be more cost-effective
612 than regenerating it; since the regeneration process can reach up to 70% of the total
613 operating and maintenance cost of an adsorption system (Goh et al., 2008). However,
614 future works should be done concerning the study of concrete adsorbent regeneration.

615

616 **3.2.8 Adsorbent and adsorption process cost assessment**

617

618 Economic study is an important factor to be taken into account for determining
619 the applicability of an adsorbent in a wastewater treatment process. The economic
620 viability of the adsorption process depends mainly on the cost of the used adsorbent.

621 However, since the concrete adsorbent is a waste, it means that there is no cost
622 associated with its preparation and with equipment for instance. Therefore, it is
623 highlighted that there will be a cost associated with the transportation of the waste to the
624 wastewater treatment plant. When it is compared to other low-cost adsorbents reported
625 in the literature, the adsorption process by using concrete waste adsorbents can be
626 economically viable since it is an abundant waste and it is not necessary to spend energy
627 and chemicals to process it. Moreover, when compared with the most popular adsorbent
628 (commercial activated carbons), it can reach 111$/kg, which is too high. However, low
629 cost activated carbons can be prepared at the cost of 14.36$/kg (Reza et al., 2014).

Bhatnagar et al., (2013) prepared a low-cost adsorbent by using a bio-waste treated with H_3PO_4 and calculated its preparation costs at 0.5 $/kg.

Therefore, to achieve a circular economy, this research shows that it is possible to use a low-cost and eco-friendly adsorbent for recovering P from aqueous effluents. To close the cycle, the P-loaded concrete can be potentially used as fertilizer which makes the process more economically sustainable.

4. Conclusion

In this work, the effect of the carbonation process on physicochemical properties and in the adsorption of phosphate on the concrete slurry powder was investigated.

General order kinetic provided the better fitting model for the adsorption behavior of P onto both non-carbonated and carbonated concrete samples. The equilibrium adsorption data were better fitted by Freundlich isotherm model describing heterogeneity in the adsorption of P onto concrete-waste adsorbents.

P removal was mainly ruled by chemical adsorption through inner-sphere complexion and P precipitation on the surface of concrete adsorbent having Ca^{2+} as an essential element in the adsorption mechanism. Compared with other phosphate adsorbents, both non-carbonated and carbonated concrete may be an economical and efficient adsorbent.

The non-carbonated sample gave a high adsorption capacity of P (47.6 mg P per g of concrete, experimental value) and presenting a fast and high initial adsorption, reaching 72% of P removal only in 5 min at 22°C, while carbonated sample showed a value of 30.6 mg g^{-1} as adsorption capacity at the same experimental conditions.

Non-carbonated and carbonated concrete adsorbents showed to have of the highest phosphate-removal performance between many adsorbents found in the literature; therefore, concrete slurries can be used widely as an inexpensive phosphate-recovery adsorbent.

Additionally, the application of non-carbonated and carbonated concrete waste, loaded with P, as potential fertilizers can be an interesting and environmentally approach for reusing this kind of waste.

The environmental analysis highlighted that the adsorbents did not leach out heavy metals above the allowable limits preconized by FAO for irrigation waters. However, aspects related to monitoring the presence and mobility of heavy metals on soil must be better addressed and monitored.

Acknowledgment

The authors thank the Coordination of Improvement of Higher Education Personnel (CAPES, Brazil) and Foundation for Research Support of the State of Rio Grande do Sul (FAPERGS), National Council for Scientific and Technological Development (CNPq, Brazil) for financial support and sponsorship. Dr Glaydson Simões dos Reis is grateful to the CAPES for the postdoctoral scholarship granted through the National Postdoctoral Program (PNPD). We are also grateful to Chemaxon for giving us an academic research license for the Marvin Sketch software, Version 19.20.0, (http://www.chemaxon.com), 2019 used for calculation of phosphate species distribution.

References

Abass A., Olajire A., 2013. A review of mineral carbonation technology in sequestration of CO_2, J. Petroleum Sci. Eng. 109, 364–392.

Alavaisha E., Manzoni S., Lindborg R., 2019. Different agricultural practices affect soil carbon, nitrogen, and phosphorous in Kilombero –Tanzania, J. Environ. Manage. 234, 159–166.

Ayers R.S., Westcot D.W., 1985. Water quality for agriculture, Food and Agriculture Organization of the United Nations, Rome, Italy.

688 Aynur K., Ulubeyli S., 2016. Current Methods for the Utilization of the Fresh Concrete
689 Waste Returned to Batching Plants, Procedia Eng. 161, 42– 46.
690 Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M. 2013. An overview of the
691 modification methods of activated carbon for its water treatment applications,
692 Chem. Eng. J. 219, 499–511
693 Bravo M., de Brito J., Evangelista L., Pacheco J., 2018. Durability and shrinkage of
694 concrete with CDW as recycled aggregates: Benefits from superplasticizer's
695 incorporation and influence of CDW composition. Construc. Build. Mater. 168,
696 818–830.
697 Burianek P., Skalicky M., Grunwald A., 2014. Phosphates adsorption from water by
698 recycled concrete. Geo. Sci. Eng. 60, 1–8.
699 Cardoso R., Silva R.V., de Brito J., Dhir R., 2016. Use of recycled aggregates from
700 construction and demolition waste in geotechnical applications: A literature
701 review. Waste Manag. 49,131–145.
702 Choi J., Chung J., Lee W., Kim J-O., 2016. Phosphorous adsorption on synthesized
703 magnetite in wastewater, J. Ind. Eng. Chem. 34, 198–203.
704 Deng Y., Wheatley A., 2018. Mechanisms of Phosphorus Removal by Recycled Crushed
705 Concrete, Int. J. Environ. Res. Public Health 15, 357.
706 dos Reis G.S., Sampaio C.H., Lima E.C., Wilhelm M., 2016. Preparation of novel
707 adsorbents based on combinations of polysiloxanes and sewage sludge to
708 remove pharmaceuticals from aqueous solutions, Colloids and Surfaces A:
709 Physicochem. Eng. Aspects 497, 304–315.
710 Egemose S., Sønderup M.J., Beinthin M.V., Reitzel K., Hoffmann C.C., Flindt M.R., 2012.
711 Crushed concrete as a phosphate-binding material: a potential new management
712 tool. J. Environ. Qual. 3, 647-53.
713 Goh K.H., Lim T.T, Dong Z., 2008. Application of layered double hydroxides for removal
714 of oxyanions: a review. Water Research 42, 1343–1368.

715 Johansson L., Gustafsson J.P., 2000. Phosphate removal using blast furnace slags and
716 Opoka-mechanism, Water Res. 34, 259–265.
717 Kasperiski F. M., Lima E.C., Umpierres C. S., dos Reis G. S., Thue P.S., Lima D.R., Dias
718 S.L.P., Saucier C., da Costa J.B., 2018. Production of porous activated carbons
719 from Caesalpinia ferrea seed pod wastes: Highly efficient removal of captopril
720 from aqueous solutions, J. Cleaner Prod. 197, 919-929.
721 Kudeyarova A.Y., 2010. Chemisorption of Phosphate Ions and Destruction of
722 Organomineral Sorbents in Acid Soils, Eurasian Soil Science 43, 635–650.
723 Leite A.J.B., Lima E.C., dos Reis G.S., Thue P.S., Saucier C., Rodembusch F.S., Dias
724 S.L.P., Umpierres C.S., Dotto G.L., 2017. Hybrid adsorbents of tannin and APTES
725 (3-aminopropyl-triethoxy-silane) and their application for the highly efficient
726 removal of acid red 1 dye from aqueous solutions, J. Environ. Chem. Eng. 5,
727 4307-4318.
728 Li F., Wu W., Li R., Fu X., 2016. Adsorption of phosphate by acid-modified fly ash and
729 palygorskite in aqueous solution: Experimental and modeling, Appl. Clay Sci.
730 132–133, 343–352.
731 Lima E.C., Adebayo M.A., Machado F.M., 2015. Kinetic and Equilibrium Models of
732 Adsorption, in: Bergmann, C.P., Machado, F.M. (Eds.), Carbon Nanomaterials as
733 Adsorbents for Environmental and Biological Applications, Springer International
734 Publishin, New York, United States pp. 33–69.
735 Littler J., Geroni J.N., Sapsford D.J., Coulton R., Griffiths A.J., 2013. Mechanisms of
736 phosphorus removal by cement-bound ochre pellets. Chemosphere 90, 1533–
737 1538.
738 Ma H., Guo Y., Qin Y., Li Y-Y., 2018. Nutrient recovery technologies integrated with
739 energy recovery by waste biomass anaerobic digestion, Bioresource Technol.
740 269, 520–531.
741 Nasar N., Payattati B., 2015. Int. J. Innovative Res. Sci. Eng. Technol, 1-8.

742 Park J.Y., Byun H.J., Choi W.H., Kang W.H., 2008. Cement paste column for
743 simultaneous removal of fluoride, phosphate, and nitrate in acidic wastewater.
744 Chemosphere 70,1429–1437.
745 Rahnemaie R., Hiemstra T., van Riemsdijk W.H., 2006. Inner- and outer-sphere
746 complexation of ions at the goethite–solution interface, J. Colloid Inter. Sci. 297,
747 379–388.
748 Reza, R.A., Ahmed, M.J.K., Ahmaruzzaman, A.K.S.M. 2014. A Non-Conventional
749 Adsorbent for the Removal of Clofibric Acid from Aqueous Phase, Sep. Sci.
750 Technol. 49, 10, 1592-1603
751 Sabah E., Majdan M., 2009. Removal of phosphorus from vegetable oil by acid-activated
752 sepiolite. J. Food Eng. 91, 423–427.
753 Sasaki T, Iizuka A., Watanabe M., Hongo T., Yamasaki A., 2014. Preparation and
754 performance of arsenate (V) adsorbents derived from concrete wastes. Waste
755 Manage. 34, 1829–1835.
756 Sun D., Hale L., Kar G., Soolanayakanahally R., Adl S., 2018. Phosphorus recovery and
757 reuse by pyrolysis: Applications for agriculture and environment, Chemosphere
758 194, 682-691.
759 Taylor H.F.W., 1978. The chemistry of cements (in spanish), Ed. URMO, Bilbao, Spain.
760 Thue P.S., Adebayo M.A., Lima E.C., Sieliechi J.M., Machado F.M., Dotto G.L., Vaghetti
761 J.C.P., Dias S.L.P., 2016. Preparation, characterization, and application of
762 microwave-assisted activated carbons from wood chips for removal of phenol
763 from aqueous solution, J. Mol. Liq. 223, 1067–1080.
764 Tracz T., Zdeb T., 2019. Effect of Hydration and Carbonation Progress on the Porosity
765 and Permeability of Cement Pastes, Materials 12, 192.
766 doi: 10.3390/ma12010192
767 Umpierres C.S., Thue P.S., dos Reis G.S., de Brum I.A.S., Lima E.C., de Alencar W.A.,
768 Dias S.L.P., Dotto G.L., 2018. Microwave activated carbons from Tucumã

(Astrocaryum aculeatum) waste for efficient removal of 2- nitrophenol from aqueous solutions. Environ. Technol. 39, 1173-1187.

Vásquez A., Cárdenas V., Robayo R.A., de Gutiérrez R.M., 2016. Geopolymer based on concrete demolition waste. Adv. Powder Technol. 27, 1173–1179.

Wamba A.G.N, Ndi S.K., Lima E.C., Kayem J.G., Thue P.S., Kayem J.G., Robembusch F.S., Dos Reis G.S., De Alencar W.S., 2017. Synthesis of grafted natural pozzolan with 3-aminopropyl-triethoxy-silane: preparation, characterization, and application for removal of Brilliant Green 1 and Reactive Black 5 from aqueous solution, Environ. Sci. Pollut. Res. 24–27, 21807–21820.

Wang X.J., Chen J.D., Kong Y.P., Shi X.M., 2014. Sequestration of phosphorus from wastewater by cement-based or alternative cementitious materials. Water Res. 62, 88–96.

World Business Council for sustainable development (WBCSD), 2019. Recycling concrete. www.docs.wbcsd.org/2009/07/CSI-RecyclingConcrete-FullReport.pdf/ (Accessed 5 July 2019)

Yan J., Kirk D.W., Jia C.Q., Liu X., 2007. Sorption of aqueous phosphorus onto bituminous and lignite coal ashes, J. Hazard. Mat.148, 395–401.

Yuan X., Xia W., An J., Yin J., Zhou X., Yang W., 2015. Kinetic and Thermodynamic Studies on the Phosphate Adsorption Removal by Dolomite Mineral, Journal of Chemistry, 853105, 1-8, DOI: 10.1155/2015/853105

Zha Z., Ren Y., Wang S., Qian Z., Yang L., Cheng P., Hana Y., Wang M., 2018. Phosphate adsorption onto thermally dehydrated aluminate cement granules, RSC Adv. 8, 19326–19334.