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Investigations on phosphorus recovery characteristics by active carbon prepared from date stones in aqueous solutions

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ABSTRACT

The efficiency of raw date stones (RDS), its derived activated carbon (DS-AC) and a commercial active carbon (AC) in recovering phosphorus (P) from aqueous solutions was investigated in batch mode under different experimental conditions. The chemical activation process using sulfuric acid (H_2SO_4) revealed that compared to RDS, the DS-AC has improved physico-chemical characteristic including a high specific surface (612 m^2/g) and an important micro-pore volume (0.27 cm^3/g). This has resulted in the increase of P adsorption capacity by about 50.5%, reaching a value of 25.2 mg/g. Moreover, the P recovery by DS-AC seems to be relatively rapid and significantly affected by the pH of the aqueous media and the presence of other ions, especially calcium. This adsorption process might be mainly chemical involving cation exchange process. Adsorption isotherms have been applied to study the P adsorption behavior and to determine the adsorption capacity of the absorbents. Regression analysis was used to study the empirical statistics of the experiments and to identify the significance of the parameters used to enhance the P adsorption capacity. This study proves that DS-AC can be considered as a promising and economic material for P ions recovery from aqueous solutions for a further subsequent use in other domains such as agriculture.

Keywords: Date stones; Activated carbon; Phosphorus; Recovery; Characteristics; Mechanism

1. Introduction

Phosphorus (P) is a common constituent of agricultural fertilizers, animal biomasses, sewage and various industrial effluents. It is a vital nutrient for crops growth and productivity. It plays important roles in cell division, reproduction, and plant metabolism [1]. The intensive utilization of P in our daily life has resulted in the production of wastewaters with relatively high concentrations [2]. The non-controlled wastewaters discharge into water bodies and the environment can speed up the eutrophication process. This process can lead to serious environmental problems like the death of aquatic organisms due to the uncontrolled growth of aquatic plants and varieties of algae

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[3]. Various technologies have been used for the uptake of P from contaminated water, such as reverse osmosis, solvent extraction, membrane separation, filtration, chemical precipitation, oxidation, reduction, coagulation, ion exchange and biological methods [4]. Though, these techniques are not cost-effective, and some of them are not environmentally friendly and do not remove the P from polluted water which makes this issue more challenging for the researchers. Compared to other techniques adsorption process has been pointed out as one of the most suitable methods to recover P from aqueous solutions because of its simplicity of use, high efficiency and economic viability, environmentally safe, and the process is non-destructive so that contaminants can be separated and recycled [5]. Various investigators have studied the sorption of P from aqueous solutions using various mineral adsorbents such as calcium silicate [6], nanoscale zero valent iron [7], marble wastes [8,9], phosphates mine wastes [10] and halloysite nanotubes [11]. Over the past decades, various raw and modified organic biomasses have been used for P recovery from aqueous solutions such as *Posidonia oceanica* fibers [12], cypress sawdust [13], and animal biomasses [14]. The synthesis of activated carbons (AC) form agricultural wastes and their use as effective adsorbents for various pollutants, including P, have been pointed out as interesting research option [15]. Compared to raw agricultural biomasses, ACs generally dispose of attractive physico-chemical properties including higher values of BET surface area, and total/micropore volumes, and richer targeted functional groups [16]. There are two essential methods to activate carbon materials; physical activation with high-temperature treatment (800–1,100°C) and chemical activation with chemical reagents (KOH, $ZnCl_2$, K_2CO_3 and H_3PO_4) [17]. However, chemical activation has some advantages over physical activation, since it promotes the development of a better porous structure [18,19]. Various biomasses have been used for ACs synthesis and applied for both mineral/organic pollutants form aqueous solutions as floating aquatic plants [20], microalgal biomass [21], biomass bottom ash [1], Eucalyptus camaldulensis [22] and palm *Phoenix dactylifera* [23]. *Phoenix dactylifera* plant is mainly cultivated in the arid and semi-arid regions of the world, particularly in the Middle East and North Africa (MENA). Tunisia is one of the largest producers of date fruits with more than 41,000 hectares and an annual production rate of about 240,000 tons [24]. As a result, large quantities of date stone wastes are generated annually since its weight represents around 11%–18% of the total date fruit weight [25]. ACs derived from date stone wastes has been efficiently used for various mineral and organic pollutants from aqueous solutions including heavy metals [26], dyes [27,28], pharmaceuticals [21], and pesticides [29]. However, only very few studies have dealt with the use of these ACs for P recovery from aqueous solutions [30]. They reported that under specific conditions, ACs may efficiently remove P from wastewaters. So far, very little attention has been paid to the role of co-existing ions and ionic strength in the P recovery process [27,31]. Therefore, the objectives of this study were to investigate the P recovery properties under wide range of experimental conditions, and to explore the main involved mechanisms in this recovery process.

2. Material and methods

2.1. Raw biomass preparation and synthesis of the activated carbon

Date stone wastes were collected from Kebili oasis (south of Tunisia) and used as a raw precursor biomass in the present study. This raw biomass was initially washed with deionized water to remove impurities, then dried at 110°C for 12 h, and finally crushed and sieved through a 500 μm mechanical sieve. The synthesis of the activated carbon consisted in the thermal carbonization of the pretreated biomass by sulfuric acid (H_2SO_4, 98%) as follows: First, 20 g of the dried raw biomass was impregnated within 100 mL of H_2SO_4 (98 wt.%) solution for 24 h at 85°C and then dried for 3 h at 105°C. The dried mixture was then carbonized by using a muffle furnace at different temperatures (400°C–700°C) and residence times (30–120 min) under a constant N_2 flow of 120 cm^3/min. Then, the activated carbon was subjected to a thorough washing with a weak alkaline solution (0.1 M NaOH), followed by a rinsing step with hot distilled water (75°C) until reaching a neutral pH. Finally, the product sample was dried at 105°C for 24 h and stored in air-tight containers.

2.2. Activated carbons characterization

The prepared activated carbons at optimum conditions were physico-chemically characterized by using different protocols and apparatus. Indeed, the pH and conductivity of the selected derived activated carbon (DS-ACs) were determined by digital pH and conductivity meter according to the experimental protocol given by Siwek et al. [32]. The ash and moisture contents were assessed by standard methods (ASTM standard, 2000). The bulk density of the DS-AC was determined according to the experimental protocol given by Menya et al. [33]. The surface areas and pore volumes were determined by through the Brunauer–Emmett–Teller (BET) approach by using N_2 adsorption isotherms at 77 K by an automatic adsorption unit (ASAP 2020). The elemental analyses (C, O, H and N) were carried out by a Thermo Fisher Flash 2000 analyzer. The pH at the point of zero charge (pH_{pzc}) was determined according to the protocol described by Letshwenyo et al. [34]. Finally, the contents of Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-} in the synthetic solutions were analyzed by liquid chromatography apparatus (Bischoff 2250 HPLC).

2.3. Phosphorus recovery experiments

In order to assess P sorption characteristics by the raw date stone wastes and the selected derived activated carbon, batch recovery experiments were carried under different experimental conditions. Potassium dihydrogen phosphate (KH_2PO_4) was used as the source of P in the synthetic wastewater. A P stock solution (100 mg/L) was prepared by dissolving 0.438 g of KH_2PO_4 in 100 mL of deionized water and used throughout this study. P recovery efficiency form aqueous solutions were carried out under batch mode (static conditions). These assays consist in shaking, at room temperature (22°C ± 2°C), 50 mL of P solutions in 120 mL capped flasks with a given mass of the used adsorbents by using a horizontal mechanical shaker. Then, the suspension was filtrated through 0.45 µm cellulose acetate filter before analysis by using the ascorbic acid method and a double-beam UV-Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at a wavelength of 868 nm. During this work, the effect of the following experimental key parameters on P recovery was investigated: (i) contact time for values of 0, 5, 10, 15, 30, 45, 60, 75 and 90 nm, (ii) initial pH for 2, 4, 6, 8 and 10, (iii) adsorbents doses for 0.5, 0.75, 1, 1.5, and 2 g/L, and (iv) P initial concentrations for 25, 50, 75, 100 and 125 mg/L.

2.4. Data analysis

The experimental data regarding the P recovery kinetic were fitted to two famous models, namely pseudo-first-order and pseudo-second-order. Similarly, the isotherm experimental data were fitted to two well-known models (Langmuir and Freundlich). The original as well as linear equations of these kinetic and isotherm models are given in the supplementary material (Table 1). The adsorbed P amount at a given moment 't', (q_t) and the related removal yield (Y_t) were assessed as follows:

$$q_t = \frac{V}{m}\left(C_0 - C_t\right) \tag{1}$$

$$Y_t = \frac{\left(C_0 - C_t\right)}{C_0} \tag{2}$$

where V is the volume of initial solution (L); m is the DS-AC and AC samples mass (g); C_0 is the initial concentration of the standard solution (mg/L) and C_t is samples solution concentration at a given time "t" (mg/L).

Moreover, the fit of isotherms models to the experimental data was analyzed by calculating the sum of squared errors (SSE) as follows:

$$\text{SSS} = \sum_{n=1}^{p}\left(q_{e,\text{theo}} - q_{e,\text{exp}}\right)_i^2 \tag{3}$$

where $q_{e,\text{exp}}$ and $q_{e,\text{theo}}$ are the measured and estimated recovered P amount (mg/g).

2.5. Statistical analysis

The P recovery assays were performed in triplicate and the mean values are given in this work. In all retained cases, the standard deviation was lower than 5% and was calculated using the Xlstat statistical software.

3. Results and discussions

3.1. Activated carbons proprieties

The main physico-chemical characteristics of the DS-AC sample are given in Table 1. Results demonstrate that the pH of DS-AC solution was slightly basic (7.2). Relatively similar value was previously reported by Dai et al. [35] for date stones collected from the same study region. Ghorbani et al. [36] reported that the pH for the most common applications of activated carbons should be between 6 and 8. The conductivity of DS-AC sample was relatively high (4.5 mS/cm) compared to the conductivity of activated carbons prepared from date stones by activation with ferric chloride (3.3 mS/cm) and zinc chloride (2.9 mS/cm) [37]. This is most probably due to the release of high contents of minerals from DS-AC samples. The moisture content of DS-AC is 10% while the ash content was 1.2%. These findings were in agreement with those reported in the literature [37,38]. Besides, the bulk density of DS-AC was 0.533 g/cm^3, which is almost the double of the lower limit (0.25 g/cm^3) suggested for granular activated carbons [39]. The DS-AC production yield (content yield) is 44%. This value is higher than that found by Hu et al. [29] for activated carbon prepared from date stones activated by phosphoric acid. On the other hand, the BET surface area and microspores volumes of DS-AC were evaluated to 612 m^2/g and 0.27 cm^3/g, respectively. The BET surface area of DS-AC was higher than various other ACs prepared from olive stones (ACOS) used by Sakamoto et al. [40] (83.72 m^2/g) and starch treated by 0.1 M of KOH (160.6 m^2/g) [41]. The high values of surface area, low ash content and high bulk density are good indicators of the suitability of this material for P from aqueous solutions. Moreover, the elemental analysis showed that the DS-AC sample was mainly formed by C and O with respective percentages of 93.2% and 5.2%. The high C content reflects a good carbonization of the raw material. Furthermore, the S content was evaluated to 1.2%. This relatively high value may be imputed to the used activating agent (H_2SO_4). In contrast, the content of N was relatively low (0.9%). It may be due to the destabilization of nitrogen functionalities during the carbonization process [42].

Table 1
Main physico-chemical properties of DS-AC sample

pH	7.19
EC (mS/cm)	4.5
Moisture content (%)	7.6
Ash content (%)	1.2
Content yield (%)	44
Bulk density (kg/m^3)	533
Specific surface (m^2/g)	612
Microspores (cm^3/g)	0.27
pH_{pzc}	7.06
N (%)	0.90
O (%)	5.15
C (%)	93.2
S (%)	1.20

3.1. Effect of contact time: kinetic study

The effect of contact time on P recovery from aqueous solutions by both AC and DS-AC was assessed under the experimental conditions given in section 2.3. Results (Fig. 1) indicate that P recovery efficiency on the AC and DS-AC increased with the increase of contact durations time. The contact time needed for P removal by AC and

DS-AC to reach equilibrium was assessedto90 min. The P amount sorption on the DS-AC and AC samples were 25.2 and 33.9 mg/g respectively. These quantities present a recovery rate of 50.5% and 67.8% of the P initial in aqueous solution. The effective P adsorption by the prepared DS-AC can be attributed to the fact that DS-AC is composed of porous structure with large internal surface area (612 m^2/g). Also as seen in Fig. 1, it is obvious that the adsorption process of P consisted of two phases: an initial rapid phase and a slower second phase and an equilibrium state. Indeed, at the beginning of the experiment, the adsorbed P amount increased rapidly until about 15 min. For periods greater than 15 min, the adsorption capacity increased but with a much slower rate. The fast adsorption process observed at earlier stage might be due to the larger accessibility to pores and large available number of vacant sites, which leads to the improvement of mass transfer driving force [43] and the strong chemical bonding between P ions and oxygenated groups in the DS-AC and AC [37]. Greater availability of various functional groups on the surface of DS-AC, which are required for interaction with ions, significantly improved the binding capacity. However, when approaching equilibrium, the P adsorbed amounts decreased, and the saturation of adsorption sites is reached [16]. In order to assess the adsorption mechanism of P onto DS-AC and AC, pseudo-first-order and pseudo-second-order kinetic models were applied and the corresponding fitted parameters are listed in Table 2.

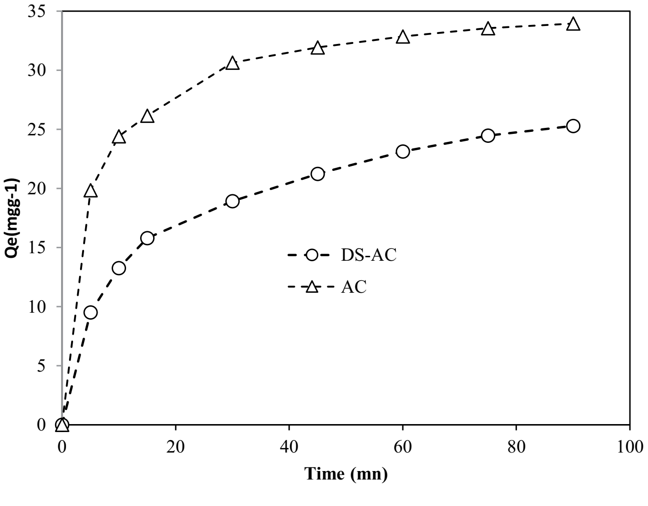

Fig. 1. Sorption kinetic P by the DS-AC and AC (dose = 0.5 g/L; T = 22°C).

Table 2
Pseudo-first-order and pseudo-second-order constants for P recovery by AC and DS-AC

	Pseudo-first-order model				Pseudo-second-order model		
	$q_{e,\text{exp}}$	R^2	K_1	$q_{e,\text{theo}}$	R^2	K_2	$q_{e,\text{theo}}$
DS-AC	25.28	0.915	1.31	21.63	0.99	0.037	26.12
AC	33.94	0.865	1.01	28.57	0.99	0.028	34.25

The correlation coefficients (R^2) of the nonlinear fitting models confirmed that the pseudo-second-order kinetic model (>0.99) was more suitable than the pseudo-first-order kinetic model (<0.92) for describing the adsorption behavior of Ponto DS-AC and AC. In addition, the experimental q_e values calculated from the pseudo-second-order model were in good agreement with the theoretical q_e values, providing further evidence for the above conclusion. It was suggested that the adsorption process was mainly a chemisorption involving the force of sharing or exchanging electrons between P and DS-AC and AC adsorbents [28]. Similar results were reported for P removal from wastewater using palm fibers [39] and date palm leaflets [6].

3.2. Effect of initial pH

The pH value of the aqueous solution is a crucial parameter in the P adsorption process. The P recovery efficiency onto DS-AC and AC for an initial pH range of 2 to 10 showed that both materials efficiently recover P for especially acidic media (Fig. 2). The P recovery yields were estimated to 55%–73% at an initial pH of 2 for DS-AC and AC, respectively. This parameter decreases to 35%–51% for an initial pH of 10 for DS-AC and AC, respectively. This behavior may be linked to the pH_{zpc} of the tested materials which have been assessed to 7.4 and 7.2 for the AC and DS-AC respectively. The surface charge of the adsorbents is positive for lower pH than pH_{zpc} which explained the relatively high adsorption capacities of the negatively charged P ions through electrostatic reactions for low initial pH values. For the pH range of 2–10 the electrostatic attraction between the negatively charged P ions and positively charged AC and DS-AC surface promotes the P adsorption. Though, with increasing pH, the number of binding sites with positive charges on AC and DS-AC decreases; thus, the electrostatic repulsion gradually increases, which hinders the P adsorption. Meanwhile, at high pH, OH^- ions compete with the negatively charged phosphates for binding sites, which reduces the P recovery efficiency. Generally, as the initial used pH was increased, the number of positively charged sites decreased and consequently, the P recovered amounts decreased. Similar results have been reported by several studies [44,45].

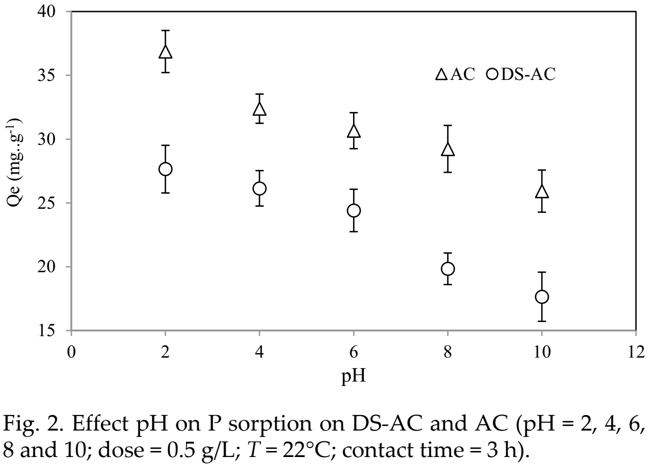

Fig. 2. Effect pH on P sorption on DS-AC and AC (pH = 2, 4, 6, 8 and 10; dose = 0.5 g/L; T = 22°C; contact time = 3 h).

3.3. Effect of adsorbents dosage

Adsorbent dose is a mainly important parameter in adsorption which determines the amount of P removal as well as the economics of process. To examine the possible effects of adsorbents doses on the P recovery by DS-AC and AC, experiments were conducted under the experimental conditions given in section 2.3. Results (Fig. 3) showed that the P removal percentage increased from 32.2% to 55.3% and from 21.4% to 48.4% when the doses of DS-AC and AC were increased from 0.5 to 2 g/L, respectively. This finding is attributed to the presence of larger availability of exchangeable sites for the P ions, that is, more active sites are available for P binding. These results are in line with other researches outcomes which revealed that adsorbent dose plays a crucial role in the adsorption method [12,46]. However, the DS-AC concentration of 2 g/L seems to be a good compromise dosage to obtain excellent adsorption with an economic cost.

3.4. Effect of phosphorus initial concentrations: adsorption isotherms

The P sorption isotherms (Fig. 4) were studied under the experimental conditions given in section 2.3. It can be clearly seen that the P recovery capacity increased with the increase of the initial P concentration. Indeed, the highest recovered amounts by DS-AC (27.61 mg/g), and AC (37.85 mg/g) were assessed for the highest initial P concentration (125 mg/L). This finding could be attributed to the increase of driving forces that are dependent on the concentration gradient between the aqueous solution and the adsorbents particles surface. Similar results were reported for various adsorbents [47,48]. The experimental results were fitted to Langmuir and Freundlich models and results are given in Table 3. It appears that Langmuir model fits better to the experimental data than the Freundlich model since it has higher regression coefficients and lower SSE values (Table 3). Furthermore, the maximum calculated P sorption amounts ($q_{\max}$) from the Langmuir isotherm were close to the experimental values, which suggested that P sorption onto the DS-AC and AC formed a monolayer [16]. Similarly, Taban et al. [49] found that the Langmuir model is the most appropriate model to describe the P adsorption onto date stones granular AC with a maximum capacity of 137.0 mg/g.

3.5. Influence of ionic strength on the P sorption

The ionic strength of effluents is an important environmental factor in large scale industrial application that significantly affects the sorption of a desired solute. The effect of ionic strength (with $CaCl_2$ as background electrolyte) on the P adsorption on DS-AC and AC was investigated using the batch method in presence of 0, 5, 25, 50, 100 and 200 mM of $CaCl_2$ and the results of the P adsorbed quantity at equilibrium as a function of electrolyte concentration is given in Fig. 5. On the basis of this figure, it can be clearly seen that the P recovery was not affected by $CaCl_2$ ionic strength for values lower than 5 mM. This indicated that P ions have higher binding affinity with the active sites than the chloride calcium ions. However, P recovery capacity decreased gradually as the ionic strength increased from 5 to 200 mM (Fig. 5). Indeed, the P adsorbed amount decreased by 22.7% and 16.6% for DS-AC and AC when the used $CaCl_2$ concentration increased from 5 to 200 mM. It appeared that the DS-AC and AC adsorbed less P in the presence of chloride

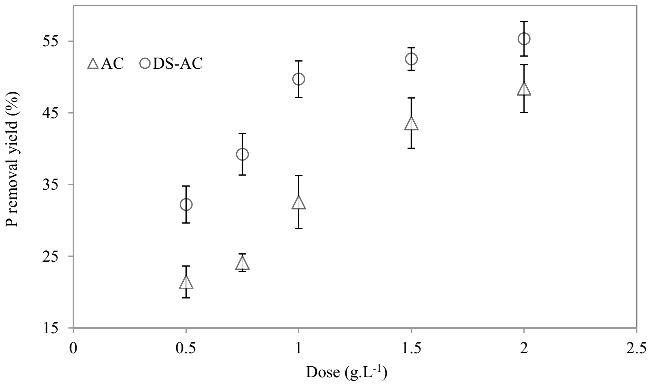

Fig. 3. Effect of dose on P sorption on DS-AC and AC (dose = 0.5, 0.1, 1.5 and 2 g/L; C_0 = 50 mg/L; T = 22°C; contact time = 3 h).

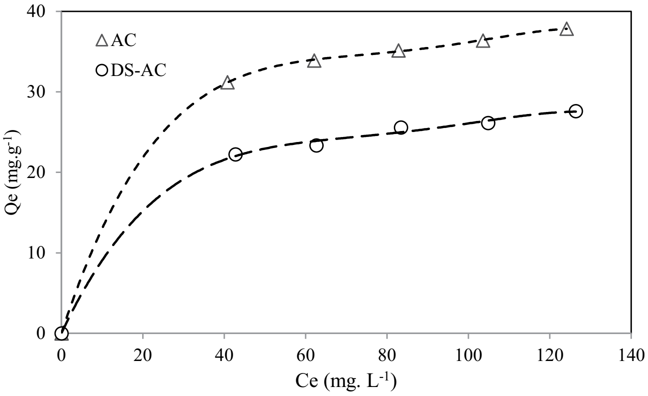

Fig. 4. Isotherm adsorption of phosphorus by the DS-AC and AC (C_0 = 25, 50, 75, 100 and 125 mg/L; T = 22°C; contact time = 3 h; dose = 0.5 g/L).

Table 3
Adsorption parameters of Freundlich and Langmuir isotherm models for P recovery by AC and DS-AC

	Freundlich model					Langmuir model			
	$q_{\exp}$	R^2	$1/n$	k_F (mg/g)	SSE	R^2	k_L	$q_{\max}$ (mg/g)	SSE
DS-AC	27.61	0.931	0.297	28.73	1.254	0.997	0.23	27.52	0.1081
AC	37.85	0.941	0.290	39.41	2.433	0.971	0.19	38.26	0.1681

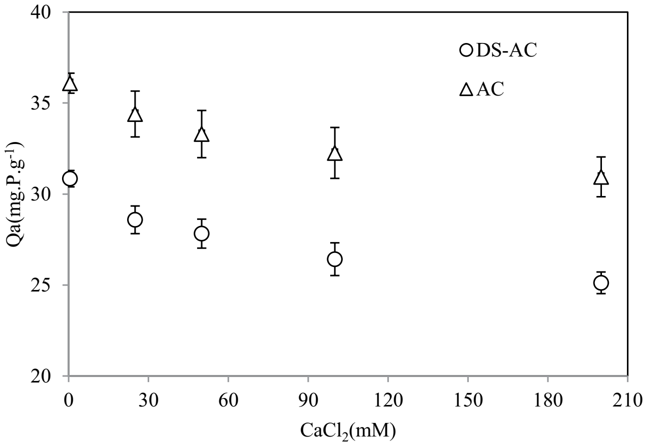

Fig. 5. Influence of $CaCl_2$ concentration on the P sorption by DS-AC and AC (0.5, 25, 50, 100 and 200 mM of $CaCl_2$; dose = 0.5 g/L; T = 22°C; time: 3 h).

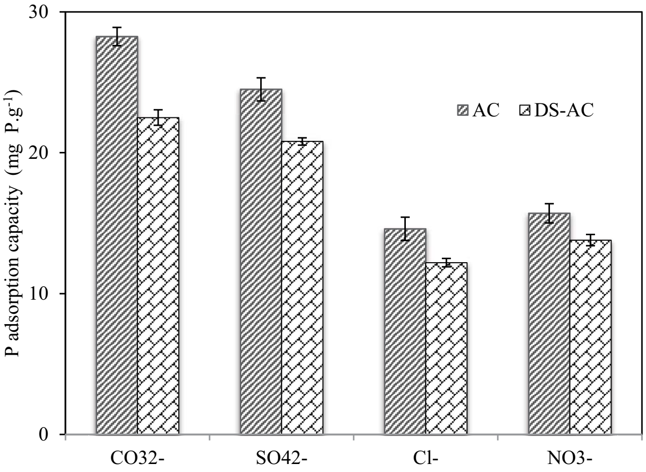

Fig. 6. Effect of co-existing anions on P sorption on DS-AC and AC adsorbent (dose = 0.5 g/L; V = 50 mL; T = 22°C; time: 3 h).

and calcium ions than the case in which no anions were added. Ion exchange reaction has been frequently proposed as a mechanism for P recovery, in which exchange occurs between P and active site loaded on the adsorbents [29]. The introduction of competing anions would reduce the P recovery capacity [30]. The recovery amount decreased with increase in the concentration of $CaCl_2$, this may be explained on the basis of ion exchange mechanism that played a significant role in the adsorption of P process. The chloride ions would compete with phosphate ions on the active sites. This result is in line with previous studies which indicated that the introduction of competing anions would reduce the sorption capacity of phosphate [50–52].

3.6. Influence of co-existing anions

In wastewaters, P ions generally co-exist with various other ions that might have adsorption competition on the adsorbents' active sorption sites. Common anions, such as Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-}, are typically chosen as the competing anions to explore the selectivity of adsorbents for P adsorption. The effect of the presence of specific anions on P recovery was assessed under the experimental conditions given in section 2.3. Results (Fig. 6) showed that the P adsorption percentage onto DS-AC decreased from 92.4% to 50.4% when Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-} are present in the system. This might be due to the adsorption competition onto the adsorbents actives sites between P anions and these artificially added ones [53,54]. Also, some anions could enhance columbic repulsion forces and compete with P for the active sites, decreasing therefore the P adsorption. Moreover, the following order $CO_3^{2-} > SO_4^{2-} > NO_3^- > Cl^-$ was found and indicated that anions with multivalent anions affect more P adsorption on DS-AC than anions with monovalent [55]. This could be expected because the divalent ions (CO_3^{2-} and SO_4^{2-}) have high negative charge densities capable of competing with P for the active sites on DS-AC. In contrast, monovalent ions (Cl^- and NO_3^-) have a lower charge and therefore small compete effectively for electrostatic interactions and affect weak P adsorption on DS-AC [56].

4. Conclusions

This study clearly shows that palm date stones could be converted into valuable activated carbon with enhanced physico-chemical properties. This allows an efficient recovery of phosphorus form aqueous solutions under wide experimental conditions of initial pH values, P concentrations, presence of other foreign anions etc. Results for DS-AC showed that pH and adsorbent dosage have significant effects on P recovery factors. The higher P recovery (27.6 mg/g) was observed as pH = 2 due to the electrostatic attraction of the positively charged adsorbent with P ions. On the other hand, higher adsorbent dosage resulted in more available binding sites for adsorption and consequently higher P recovery yields. The highest obtained P recovery was 55.3% at a dosage of 2 mg for DS-AC/mL P solution. However, P recovery capacity decreased by 22.7% when the used $CaCl_2$ concentration increased from 5 mM to 200 mM and by 92.4% to 50.4% when Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-} are present in the system. Langmuir isotherm was found to be the isotherm that best describes the adsorption of P onto DS-AC. The DS-AC material was found to have a slightly inferior P recovery compared to AC based on, however, its low cost and the positive environmental implications of using a renewable source for the production of such adsorbent is more beneficial. Also, this P-loaded material can be reused in a context of circular economy as eco-friendly biofertilizer in poor agricultural soils. Further investigations should be carried out in order to: (i) optimize the P recovery process under dynamic conditions (laboratory columns) which is close to the reality, (ii) the study of the P release slowness and its assimilation by local and typical plants. An important attention will be paid to the bio-physico-chemical reactions in the subsurface during the valorization of these P-loaded materials.

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