

# Mineral ions adsorption at low and middle concentrations onto grinded and dried of *Carpobrotus edulis* plant as new adsorbent

Mohamed CHIBAN<sup>1\*</sup>, Amina SOUDANI<sup>1</sup>, Hassan KABLI<sup>1</sup>, Fouad SINAN<sup>1</sup>, Michel PERSIN<sup>2</sup>.

1: Equipe de Matériaux, Photocatalyse et Environnement, Faculté des Sciences d'Agadir, BP. 8106 Cité Dakhla, Maroc

2 : Institut Européen des Membranes, CRNS N° 5635, 1919 Route de Mende, 34293 - Montpellier Cedex 5, France.

\*: Correspondance. : E-mail, [mmchiban@yahoo.fr](mailto:mmchiban@yahoo.fr), Tel: + 212 (0)28 22 09 57. Fax : + 212 (0)48 22 01 00.

## Abstract:

In the present study, the removal of mineral ions from aqueous solution by adsorption was studied. The adsorbent used in the present work was obtained from ground dried of *C. edulis* plant grown in south-western Morocco. The efficiency of the *C. edulis* plant particles was investigated using batch adsorption technique under different experiment conditions by varying parameters such as the contact time, the initial anions concentrations, the temperature and the initial solution pH. The equilibrium time was found to be 30, 240 minutes for  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  ions respectively. The increase of temperature increase of adsorption capacity, which also increases with decreasing solution pH. The optimum pH and temperature for adsorption in studied pH and temperature ranges were found as 2 and 35 °C, respectively for an initial anions concentration of 100 mg/l. The adsorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  ions by *C. edulis* plant particles increased with increasing initial concentration. The adsorption capacity was depending on the type of ions (atomic weight, ionic radius, structure). The adsorption data were analyzed using the Langmuir, Freundlich and Temkin adsorption isotherms to determine the mechanistic parameters related to the adsorption process. The results generally showed that these *C. edulis* plant particles could be considered as a potential adsorbent material the removal of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  ions from aqueous solutions.

**Key words:** *C. edulis* plant particles, Ionic adsorption, adsorption isotherm, wastewater treatment.

## Introduction

Several phosphorus and nitrogen compounds, including orthophosphates and nitrate have been frequently present in drinking water and various types of agricultural, domestic and industrial wastewater [Peavy (1985), Lin (1996)]. Nitrate and phosphate can stimulate eutrophication where pollution is caused in waterways by heavy algal growth, as they are both rate-limiting nutrients for the process. Nitrate contaminated water supplies have also been linked outbreaks of infectious disease [Barber (2000)]. Excess nitrate in drinking water may methemoglobinaemia also called a blue baby disease, in newborn infants [Feleke (2002), Arden (1994)].

Previous work [Cohen (1991, 1992), Sinan (1995)] concerning ionic adsorption have demonstrated the involvement of specific adsorption of selenium as selenite anions  $\text{SeO}_3^{2-}$  onto a polymer surface in the cases of polyethylene oxide (POE) and the polypeptide D,L polyalanine. In the case of the very hydrophilic POE, which is adsorbed at a mercury interface as flat species under the form of a monomolecular layer, this specific adsorption has been attributed to the existence of closed distances between two oxygen atoms of the selenite

anion structure and the two oxygen atoms of two neighbouring water molecules. Similarly in the case of polyalanine, the enhanced  $\text{SeO}_3^{2-}$  adsorption has been explained as based on the ability of this polypeptide to adopt a favouring conformation, allowing closed distances between two neighbouring nitrogen atoms of the adsorbed polypeptide chain and two oxygen atoms of the selenite ion.

F. Sinan and col. [Sinan (1995a), Benhima (2008, 2003, 2002), Chiban (2005)] developed similar studies with inert solid biomaterials (dry of plants) rich on these types of biomolecules and other biomolecules (Alkaloids, Terpenes, phenolic compounds, Saponines ....) would contain the sites responsible for ionic adsorption, such as functional groups:  $-\text{COOH}$ ,  $\text{N-H}$  -  $\text{OH}$ . With minerals ions, the heavy metals are also studied, towards applications to the treatment of wastewaters. Other plants such as *Peuraria lobata ohwi* (Kudzu) [Brown (2001)], *Echornia Speciosa* (Nile rose) [Abdel-Halim (2003)], *Cupressus sempervirens* (cypress), *Eucalyptus longifolia* (cinchona) and *Pinus halepensis* (pine) [Al-Subu (2002), Salim (1994)] have been used for adsorption of the following metals:  $\text{Cu(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Zn(II)}$  and  $\text{Pb(II)}$ .

Previous work concerning phosphate and nitrate ions adsorption on different adsorbents have shown the role played by organic matter in such adsorption and especially the strong interaction between the organic matter and the orthophosphates or nitrate ions [Öztürk (2004), Akkurt (2002), Wasik (2001), Rabah (2004), Soner Altundogan (2001), Yildiz (2004), Heikkinen (1995)].

In this study,  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  removal from single ion solutions by adsorption onto dried *C. edulis* plant as new adsorbent was investigated. Toward this aim, the effect of various parameters on the adsorption process such as particles size, contact time, temperature, pH and initial concentration has been investigated.

## Materials and methods

### 1. Materials

The adsorbent used in the present work was obtained from ground dried of *Carpobrotus edulis* plant (Agadir, Morocco). They are known to have a rich polypeptides content, the importance in which the ion binding has been demonstrated in previous work [Sinan (1995a, 1995b)]. These polypeptides and other biomolecules (Alkaloids, Terpenes, phenolic compounds, Saponines ....) would contain the sites responsible for ionic adsorption, such as functional groups:  $-\text{COOH}$ ,  $\text{N-H}$  -  $\text{OH}$  [Sinan (1995a), Benhima (2008, 2003, 2002), Chiban (2005, 2007), Kuyucak (1972), Friedman (1988)]. The adsorbent obtained from *C. edulis* plant are also known to be non toxic as some of them are used in medical treatments [Couplan (1994), Paris (1965), Charnot (1945), Montilia (1990), Ahmad (1990)], making them good candidates for such processes in view of the production of drinkable water and/or water for reuse in agriculture or domestic applications. Their selection was made in relation to their relative abundance in the Mediterranean zones where they are considered as a worthless matter. The grinded plant matter used for this study is constituted of fragments increasingly of less spherical the mean diameter being lower or equal to  $500\ \mu\text{m}$ . The specific surface area of *C. edulis* particles was measured using the  $\text{N}_2$  - BET (Brunauer, Emmett, Teller) method and is found to be  $2.6\ \text{m}^2/\text{g}$ .

Aqueous solutions of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  ions were prepared by dissolving the desired quantity of  $\text{NaH}_2\text{PO}_4$  and  $\text{KNO}_3$  salts in doubly distilled water ( $18.5\ \text{M}\Omega/\text{cm}$ ).  $\text{NaH}_2\text{PO}_4$  and  $\text{KNO}_3$  salts were analytical grade reagents from Fluka. The pH of the medium was  $\text{pH} \sim 5$  for  $\text{H}_2\text{PO}_4^-$  and  $\text{pH} \sim 5.76$  for  $\text{NO}_3^-$  ion solutions.

## 2. Adsorption studies

In batch adsorption experiments, without liquid flow across a bed of particles, 40 ml of a solution at concentration  $C_1$  was mixed with 1 gram of dried and grinded of *C. edulis* plant without any pre-treatment, the mixture being vigorously stirred by use of a magnetic stirrer.

The solutions put in contact with the plant matter are maintained at a constant temperature in water bath thermostat. The time needed to reach adsorption equilibrium for a given initial ionic concentration was determined by sampling aliquots of solution analyzed during periods of 24h. The sampled solutions were centrifuged at 5000 rpm for 15 min with a Biofuge model centrifugation machine Heraeus Instruments.

The hydrogen-phosphate ions concentration was determined by formation of ammonia phosphomolybdate and subsequent reduction with ascorbic acid, followed by spectrophotometric measurement from their near IR optical absorption at 880 nm APHA (1995), with a HP model 8453 spectrophotometer (10mm optical path). The  $\text{NO}_3^-$  ions were measured a spectrophotometer (CECIL/CE 1021 at 537 nm) as per the procedures reported in [Lestage (1986)].

Adsorption of 100 mg/l of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  ions in solution by different adsorbent doses (0.25 – 2 mg/ 40 ml) for *C. edulis* particles was carried out at the natural pH.

Adsorption experiments for the effect of solution pH were conducted as follows: 1 g of grinded of *C. edulis* plant was suspended in 40 mL of  $\text{NO}_3^-$  (or  $\text{H}_2\text{PO}_4^-$  ions) solutions containing 100 mg/l for *C. edulis*. The pH of the solution was adjusted to 2–6 using 1 M HCl or 1 M NaOH solutions. The effect of temperature was studied in the temperature range between 20 °C and 40 °C. Adsorption isotherm studies were conducted by adding 1 g of *C. edulis* in solution containing 40 mL with various concentrations of each ion. The initial anions concentrations used varying between 15 to 400 mg/L.

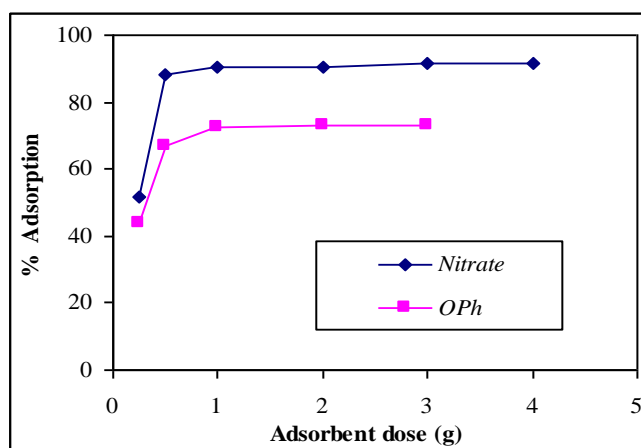
The variation of the adsorbed ions concentration ( $C_r$ ) represented in the figures is defined as  $C_r = C_0 - C_e$  for the ratio 25 g/l of mass/solution, and the removal percentage of anions from aqueous solution on grinded of *C. edulis* plant was calculated by : % Adsorption =  $[(C_0 - C_e)/C_0] \times 100$  %, where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of anions solution (mg/l), respectively.

The capacity (mg/g) of anions adsorbed from aqueous solution by *C. edulis* particles was calculated such :  $Q_r = (C_0 - C_e) \times V/m$ , where V is the total solution volume (ml), m the weight of *C. edulis* particles (g).

## Results and discussion

### 1. Effect of adsorbent dosage

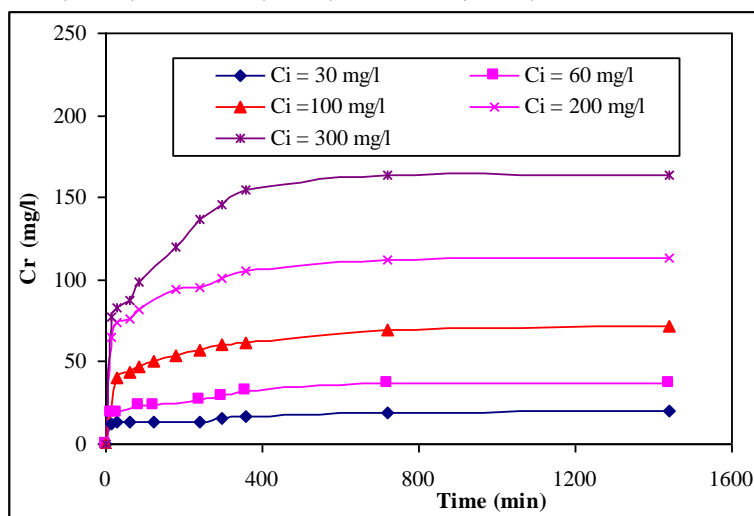
The ratio of the weight of *C. edulis* plant particles adsorbent to the volume of the aqueous phase is a very important parameter in the adsorption process. Different weight of *C. edulis* particles were shaken with 40 ml of anion solutions ( $C_1 = 100$  mg/l) for 24 hours. Figure 1 indicates the effect of amount of dried and grinded of *C. edulis* plant on % adsorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  ions. Percent adsorption increases very rapidly up to 70 - 90% by increasing amount of the adsorbent from 0.25 to 1 g and stays almost constant up to 3 g of *C. edulis* plant particles adsorbent. The amount of *C. edulis* plant particles for further adsorption experiments was selected as 1g.



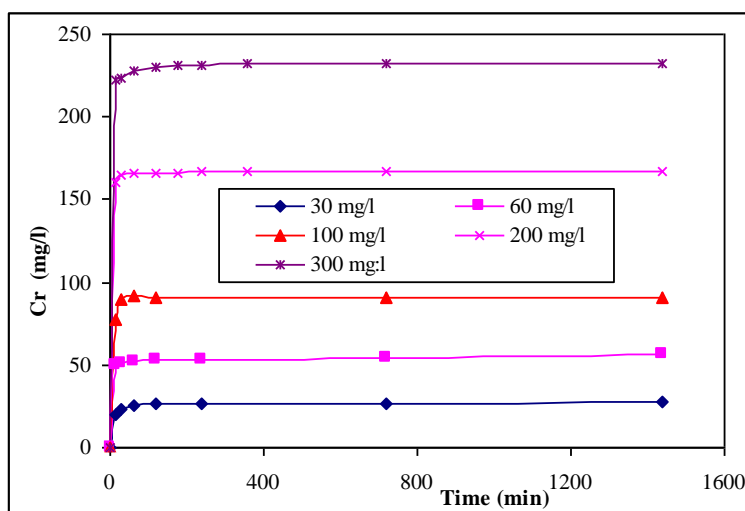
**Figure 1 :** Effect of adsorbent dose on percent adsorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  (OPh) ions. ( $T_c = 24\text{h}$ ,  $C_i = 100\text{ mg/l}$ ,  $T = 25^\circ\text{C}$  and at natural pH).

## 2. Effect of contact time and initial concentration

The effect of contact time and initial concentration on the removal efficiency of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  ions by *C. edulis* particles is illustrated in Figures 2 and 3, respectively. The concentration of nitrate and orthophosphate ions adsorbed (mg/l) by adsorbent onto their particle surface increased with the increasing of the contact time and remained nearly constant after equilibrium time. The variation with contact time of  $\text{H}_2\text{PO}_4^-$  ions (figure 2) is composed of two regimes. A quasi linear behavior in the short time domain followed by a bending for longer times tending to an adsorption steady state. In the first minutes of contact with the *C. edulis* an important percentage of the orthophosphate ions are retained. The second step is slower than the previous one and corresponds to the rate limiting step of the adsorption process. The diffusion of the orthophosphate ions towards the adsorption sites buried in the *C. edulis* particles inner structure is presumably responsible for this slow adsorption regime. From these results (figure 3), we note that, for low contact time, the nitrate adsorption by grinded of *C. edulis* plant is very quickly than the orthophosphate ions adsorption. The values of equilibrium time for *C. edulis* adsorbent were found to be about 240 minutes for  $\text{H}_2\text{PO}_4^-$  and 30 minutes for  $\text{NO}_3^-$  ions. These results are similar to those reported for the adsorption of orthophosphate and nitrate ions from real wastewaters and laboratory solution using other biomaterials [Chiban (2005), Öztürk (2004), Chiban (2006)].



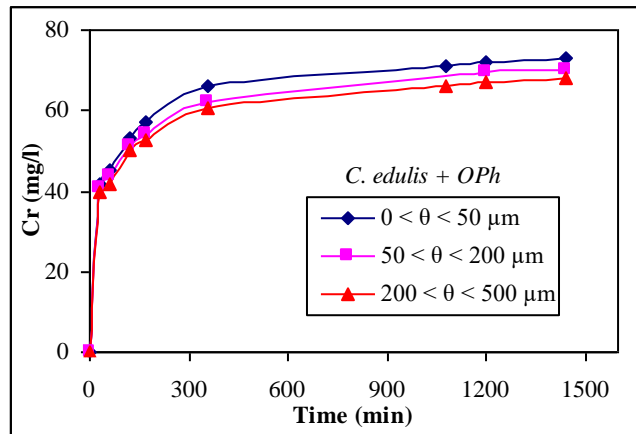
**Figure 2 :** Effect of contact time and initial concentration on the removal of  $\text{H}_2\text{PO}_4^-$  ions by *C. edulis* plant : ( $m/v = 25\text{g/l}$ ,  $T = 25^\circ\text{C}$ ,  $\text{pH} \sim 5$ ).



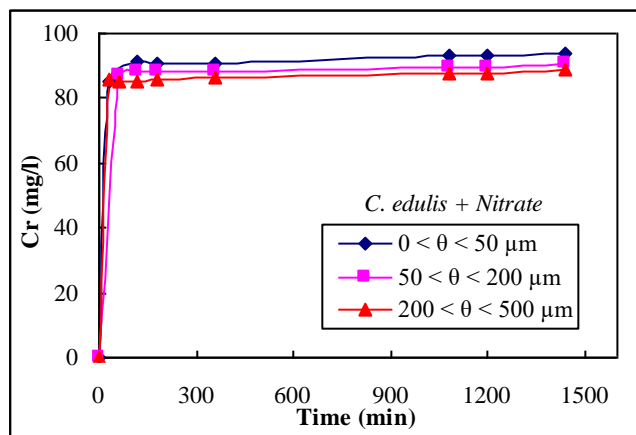
**Figure 3 :** Effect of contact time and initial concentration on the removal of  $\text{NO}_3^-$  ions by *C. edulis* plant : ( $m/v = 25\text{g/l}$ ,  $T = 25^\circ\text{C}$ ,  $\text{pH} \sim 5.76$ ).

### 3. Effect of particle size

Generally, larger particles have a longer transport distance in the particle pores for adsorption of ions. Therefore, the particle size influences the adsorption kinetics. In this study, the effect of tree size fractions of *C. edulis* particles ( $0 < \theta < 50 \mu\text{m}$ ,  $50 < \theta < 200 \mu\text{m}$  and  $200 < \theta < 500 \mu\text{m}$ ) on the adsorption kinetics of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  anions was investigated (figures 4 and 5). With increasing the particles size of the adsorbent, the uptake of both anions per unit of mass of *C. edulis* plant particles decreased during a relatively shorter period of time of adsorption. These results seem to show that the particle size influences slightly the adsorption process, and that the increase in the area per unit of weight of the sorbent by a factor of 100 at the maximum when decreasing the particle size, has a very limited effect on the adsorption. This observation is probably in relation to a relatively high specific area of porous *C. edulis* particles. The change in the particle area due to diameter variation from 50 to 500  $\mu\text{m}$ , represents to some extent a limited external surface area variation compared to the mean actual value of the specific area of the particles. Nitrogen adsorption experiments (BET), although not well suited for the evaluation of the specific area of *C. edulis* have given values close to  $2,6 \text{ m}^2/\text{g}$  whatever the particle size. The external surface area increases 100 times from the largest to the finest particles and the internal area should not change drastically with the particle size taking into account the globally structural homogeneity of the plant matter at the micrometry scale. We can conclude that internal area of *C. edulis* is mainly related to the weight of *C. edulis* particles and does not change too much with the particle size. Thus, the inner surface sites play the main active role into the anion removal and the external area has no significant role in the anion retention.



**Figure 4:** Effect of *C. edulis* particles size ( $\theta$ ) on uptake of  $H_2PO_4^-$  ions ( $m/v = 25$  g/l,  $T_c = 24h$ ,  $T = 25$  °C,  $pH \sim 5$  and  $C_I = 100$  mg/l).

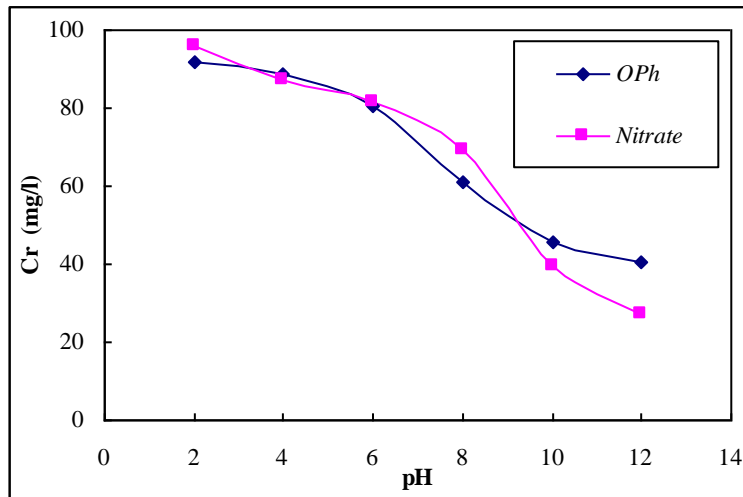


**Figure 5.** Effect of *C. edulis* particle size ( $\theta$ ) on uptake of  $NO_3^-$  ions ( $m/v = 25$  g/l,  $T_c = 24h$ ,  $T = 25$  °C,  $pH \sim 5.76$  and  $C_I = 100$  mg/l).

#### 4. Effect of pH in solution

For the removal of orthophosphate and nitrate ions from aqueous solution by adsorption process, pH is considered to be an important parameter [Wasik (2001), Savas Kopal (2002)]. Figure 6 show that the effect of solution pH on the equilibrium concentration of  $NO_3^-$  and  $H_2PO_4^-$  ions between pH 2 and 12 at 25°C and at fixed initial concentration of adsorption ions (i.e. 100 mg/l).

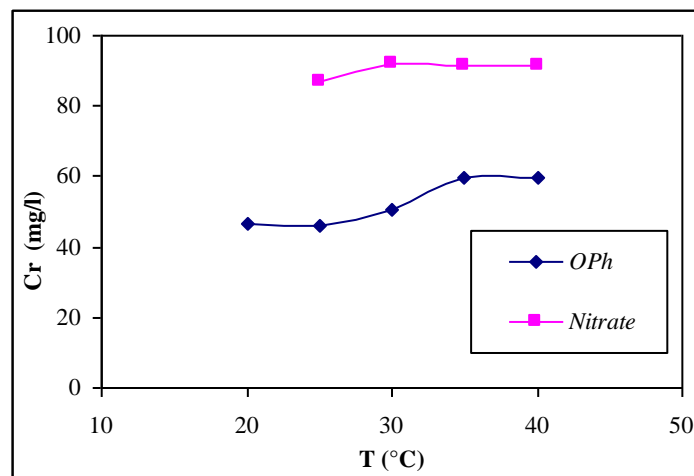
It is clear from this figure that with the increase of pH the concentration adsorbed at equilibrium of mineral ions decreases for each system. The optimum pH of adsorption was found to be 2 between the studied pH ranges. These observations suggest the involvement of hydroxide ions in the adsorption process. The pH effect may be explained in relation to the competition effect between the hydroxide ions and mineral ions.  $NO_3^-$  and  $H_2PO_4^-$  ions that could associate with the adsorbent would have to compete with the  $OH^-$  ions for the active sites. At high pH values, the concentration of  $OH^-$  ions far exceeds that of the mineral ions; hence these are bound to the adsorbent, leaving the mineral ions unbound. When the pH is decreased, the concentration of hydroxide ions decreases and the negatively charged mineral ions adsorb on the free binding sites. Similar finding have been reported in orthophosphate and nitrate adsorption studies performed using various biomaterials [Cengeloglu (2006), Öztürk (2004), Oguz (2004)].



**Figure 6 :** Effect of pH on the removal of  $H_2PO_4^-$  and  $NO_3^-$  ions by *C. edulis* plant. ( $m/v = 25g/l$ ,  $T_c = 24h$ ,  $C_i=100 mg/l$ ,  $T= 25^\circ C$ ).

### 5. Effect of temperature

The effect of temperature on the anions adsorption by these adsorbent were studied at 20, 25, 30, 35, 40 °C at 100 mg/l initial anions concentration and at natural pH. The results obtained were plotted in figure 7. From these results, the concentration of orthophosphate and nitrate ions adsorbed at different temperatures indicated the removal of these ions increases with increasing of the temperature. These results indicated also that the adsorption process of anions studied was endothermic. The  $NO_3^-$  adsorption capacity of *C. edulis* plant is not influenced by the temperature. The optimum temperature for adsorption in studied temperature was found as 35°C.



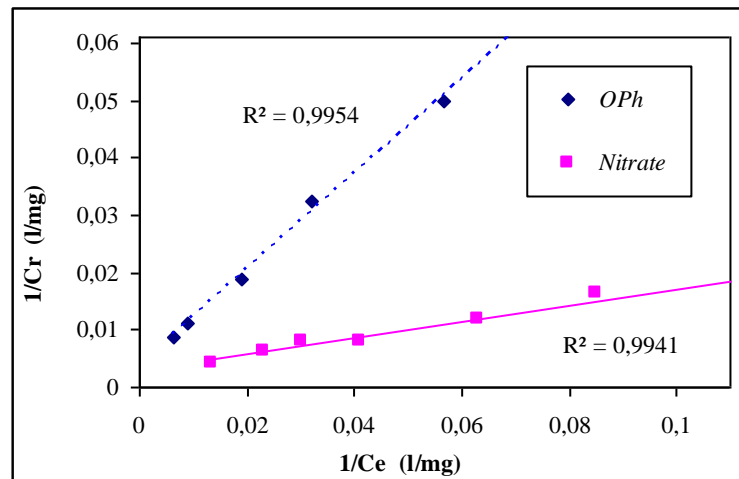
**Figure 7 :** Effect of temperature on the removal of  $H_2PO_4^-$  and  $NO_3^-$  ions by *C. edulis* plant. ( $m/v = 25g/l$ ,  $T_c = 24h$ ,  $C_i=100 mg/l$  and at natural pH).

### 6. Adsorption isotherms

The adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption gives the capacity of the adsorbent. It is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationship between adsorbent and

adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. In order to investigate the adsorption isotherm, three equilibrium models were analyzed in this work. These included the Langmuir ( $1/C_r = f(1/C_e)$ ), the Freundlich ( $\ln C_r = f(\ln C_e)$ ) and the Temkin ( $C_r = f(\ln C_e)$ ) isotherm equations.

For determining the adsorption isotherms of *C. edulis* plant, the process was carried out with initial concentration of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  between 15 and 400 mg/l at 25 °C and at normal pH. The plots corresponding to the Langmuir isotherm of nitrate and orthophosphate ions show a good correlation in all cases (figure 8). The parameters and correlation coefficients from Langmuir, Freundlich and Temkin isotherms are given in table 1.



**Figure 8 :** Langmuir plot for adsorption of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  ions by *C. edulis* plant. ( $m/V = 25 \text{ g/l}$ , Time ( $T_c$ ) = 24h,  $T = 25^\circ\text{C}$  and natural pH).

**Table 1 :** Parameters of Langmuir, Freundlich and Temkin isotherms for adsorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  ions on *C. edulis* plant:

( $m/V = 25 \text{ g/l}$ ,  $T_c = 24\text{h}$ ,  $T = 25^\circ\text{C}$  and at natural pH).

Anions	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	$Q_{\max}$	K	$R^2$	$1/n_f$	$K_f$	$R^2$	$K_t$	G	$R^2$
$\text{H}_2\text{PO}_4^-$	9.523	0.005	0.995	0.789	0.059	0.971	49.812	> 0	0.947
$\text{NO}_3^-$	12.90	0.022	0.994	0.994	0.203	0.983	102.84	> 0	0.873

These results show that the retention of orthophosphate and nitrate ions onto *C. edulis* follows the model independent adsorption sites (Langmuir isotherm) as the Freundlich model apply too, that suggests the existence of several kinds of adsorption sites ( $g > 0$ ).

## 7. Comparison of results with the literature

The orthophosphate and nitrate adsorption capacity of grinded and dried *C. edulis* plant was compared to the adsorption capacities of some other adsorbents reported in literature (Table 2). Differences of orthophosphate and nitrate uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.



**Table 2** : Comparison between the results of this work and the literature.

Anions	Matériaux	Q <sub>r max</sub> (mg/g)	Source
Orthophosphate	fly ash	6.6	Agyei (2002)
	Iron Oxyde	8	Zeng (2004)
	Montmorillinite	3.2	Jiang (2003)
	Naturel Palygorsite	4	Ye (2006)
	Modified Palygorsite	9	Ye (2006)
	<i>C. edulis</i>	9.5	This work
Nitrate	Activated carbon	4.14	Ozturk (2004)
	Sepiolete	3.46	Ozturk (2004)
	Sepiolete activated by HCl	9.8	Ozturk (2004)
	<i>C. edulis</i>	12.9	This work

For orthophosphate, the *C. edulis* plant has a greater capacity than fly ash [Agyei (2002)], Montmorillinite [Jiang (2003)] and Naturel Palygorsite [Ye (2006)], comparable to Iron Oxyde [Zeng (2004)], and Modified Palygorsite [Ye (2006)]. For nitrate, the adsorption capacities found in this work were significantly higher than reported elsewhere [Ozturk (2004)]. It is evident that the adsorption affinity of *C. edulis* towards  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  is comparable or more to other available adsorbents.

## Conclusion

The results of this study indicate that dried *C. edulis* plant particles is an effective adsorbent for removal of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  from aqueous solution. It was found that the concentration of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  adsorbed onto *C. edulis* plant particles comparatively depends on pH, temperature, contact time and initial concentration in solution. The optimum pH and temperature for adsorption in studied pH and temperature ranges were found as 2 and 35 °C, respectively. At equilibrium, the adsorption capacity of micro-particles of dry *C. edulis* plant was found to be 12.90 mg/g for  $\text{NO}_3^-$  and 9.52 mg/g for  $\text{H}_2\text{PO}_4^-$ . In addition, the adsorption capacity was depending on the type of anions (atomic weight, ionic radius, structure).

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