

Wastewater treatment by adsorption onto *Carpobrotus edulis* used as natural adsorbent

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ABSTRACT

The aim of the present paper is to study the efficiency of a new process for wastewater treatment by adsorption onto micro-particles of dry plant using the batch equilibration technique. These micro-particles are obtained from grinded and dried *Carpobrotus edulis* plant. The results show that the micro-particles of *C. edulis* plant present a good retention of heavy metals, nitrate and phosphate ions from real wastewater. This retention increased with increasing of contact time. The removal percentage of heavy metals from industrial wastewater by *C. edulis* particles was 94 % for Cd(II), 91 % for Cu(II), 99 % for Pb(II) and 98% for Zn(II). The maximum adsorption capacity was depending on the type of ions (atomic weight, ionic radius and structure...). The results indicate that the chemical oxygen demand (COD) values decrease after contact with micro-particles of dry *C. edulis* plant. The results obtained are compared with those obtained from -i) distilled water and -ii) from laboratory solutions with various concentrations. These results indicate that the micro-particles obtained from grinded and dried *C. edulis* plant could be used for removal of heavy metals and pollutant minerals from wastewater.

Key words: micro-particles of *C. edulis* plant, adsorption, wastewater treatment, heavy metals.

INTRODUCTION

Several industrial wastewater streams may contain heavy metals such as Cd, Cr, Cu, Pb, Zn, etc. including the waste liquids generated by metal finishing or the mineral processing industries. The toxic metals must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment. In recent years, the removal of heavy metal from sewage, industrial and miningwaste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, and reverse osmosis. Most of these methods suffer from some drawbacks such as high capital and operational costs, incomplete metal removal, low selectivity, high energy requirements. New approaches for removing metals based on biosorption using algae or bacteria have been reported [Dos Santos (2000), Madrid (1998)]. Although these materials present binding sites, including amines, carboxyl and thiol groups, their use for effluent treatment purposes may not be suitable due to their poor natural abundance. On the other hand, the use of other natural materials, such as peanut shells, soybean hulls and corncobs, which are available in large quantities, may present higher potentials as inexpensive sorbents for wastewater treatment [Marshall (1999), Wafwoyo (1999), Vaughan (2001)]. In addition, although the use of these materials is still not very common, in

general, they present good adsorption capacity [Dushenkov (1995), Bailey (1999)] have presented an interesting review, which focuses on the potential of a wide variety of low cost sorbents for heavy metals. According to these authors, a low cost sorbent can be assumed if it requires less prior processing, is abundant in nature, or is either a by-product or waste material from another industry. These materials could be alternatives for expensive treatment processes. In this sense, various natural materials can be used for these purposes.

The adsorption of heavy metals, nitrate and orthophosphates by these particles of *C. edulis* plant might be mainly attributed to their protein, carbohydrates and phenolic compound contents [Benhima (2002), Chiban (2007b)], containing metal-binding functional groups like carboxyl, hydroxyl, sulfate, phosphate and amino groups [Benhima (2001, 2003), Amzeghal (2003), Friedman (1972), Chiban (2007a)]. The spatial distribution of these binding groups in the *C. edulis* plant is not well resolved. The grinded and dried plant selected for this study grown in Mediterranean zones (South–Western Morocco). The micro-particles of *C. edulis* plant are known to be non toxic as these particles are used in medical treatments [Charnot (1945), Montilia (1990), Ahmad (1990)] making them good candidates for the development of processes aimed to be used in agriculture or domestic applications. Their choice was based on their relative abundance in various zones of Morocco and their quasi absence of commercial value. Recently, researchers also looked for sorbents issued from agricultural and forestry sources. For example, Brown and col. (2001) used *Peuraria lobata ohwi* (Kudzu) as sorbent to remove various heavy metal ions such as cadmium, copper and zinc from aqueous solutions, Reddad and col. (2002) used sugar beet pulp for the removal of nickel and copper ions, Abdel-Halim and col. (2003) used *Echornia Speciosa* (Nile rose) for the removal of lead ions, and Al-Subu and Salim and col. (2002, 1994) used *Cupressus sempervirens* (cypress), *Eucalyptus longifolia* (cinchona) and *Pinus halepensis* (pine) for the removal of lead, aluminium and cadmium ions. Generally these biomaterials showed a good efficiency for the treatment of polluted liquid media.

The aim of the present paper is to study the efficiency of a new process for wastewater treatment by adsorption onto micro-particles of dry plant using the batch equilibration technique. These micro-particles of dry plant are obtained from *Carpobrotus edulis* plant.

MATERIALS AND METHODS

1. Materials

The adsorbents used in this study were obtained from ground dried plant obtained from *Carpobrotus edulis* plant as previously reported in our work elsewhere [Chiban (2007b, 2006, 2005), Benhima (2008, 2003)]. A recent screening [Chiban (2007a, 2007b)] for chemical composition and surface characterization has shown that the major functional groups on *C. edulis* plant are polar hydroxyl, aldehydic and carboxylic groups. These groups has made *C. edulis* plant to have great potential as an adsorbent for metal ions in aqueous solutions. These micro-particles of *C. edulis* plant are also known to be non toxic [Charnot (1945), Montilia (1990), Ahmad (1990)]. 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 μm . The specific surface of the *C. edulis* particles was determined by the N₂/BET method (Micromeritics ASAP 2010) and found to be 2.6 m²/g. the surface structure, morphology and the elements of *C. edulis* particles were measured by scanning electron microscope

(HITACHI S-4500) (Institut Européen des Membranes de Montpellier en France) and SEM/EDX analysis (LEICA-S-260 (Institut Européen des Membranes – Montpellier - France)).

Several wastewater samples were collected and stored in polyethylene bottles from two zones of Agadir of Morocco: domestic and industrial zones. These samples were decanted and filtered on paper of 0.45 μm porosity. The pollutant charge of wastewater samples has been determined. The pH values of the wastewater samples were measured by a Mettler-Toledo meter (MP 120).

All glassware and sample bottles were washed with a detergent solution, rinsed with tap water, soaked with 1.0% subboiled HNO_3 for at least 12 h, and finally rinsed with Milli-Q water three times.

The pollutants treated wastewaters were analyzed with:

- Varian model 220 FS atomic absorption spectrophotometer for metal ions.
- HP model spectrophotometer for orthophosphate.
- HACH model spectrophotometer for chemical oxygen demand (COD).
- Waters model capillary electrophoreses for nitrates.

2. Batch adsorption experiments

Adsorption studies were carried out by batch process. 40 ml of a wastewater solution of a given metal cations (or pollutant minerals) at concentration C_i was mixed with a one gram of dried and grinded plant without any pre-treatment. The solutions put in contact with the plant matter were maintained at a constant temperature of 25°C in a water bath thermostat, the mixture being vigorously stirred by means of a magnetic stirrer. The sampled solutions were centrifuged at 5000 rpm for 15 min with a Biofuge model centrifugation machine, Heraeus Instruments.

The variation of the adsorbed ions concentration (C_r) represented in the figures is defined as $C_r = C_0 - C_f$ for the ratio 25 g/l of mass/solution, and the removal percentage of pollutant from wastewater (E) on micro-particles of *C. edulis* plant was calculated from

$$E(\%) = \frac{C_0 - C_f}{C_0} \times 100$$

where C_0 and C_f are the initial and equilibrium concentration of pollutant solution (mg/l), respectively.

The capacity (mg/g) of pollutants adsorbed from wastewaters by micro-particles of *C. edulis* plant was calculated from

$$q_a = \frac{C_0 - C_f}{m} \times v$$

where V is the total solution volume (ml), m the weight of the biomaterials (g).

RESULTS AND DISCUSSION

1. *C. edulis* characterisation

Surface morphology of the adsorbents was analyzed by scanning electronic microscopy (SEM, HITACHI S-4500) and by SEM coupled with energy dispersive X-ray analysis (EDX, LEICA-S-260).

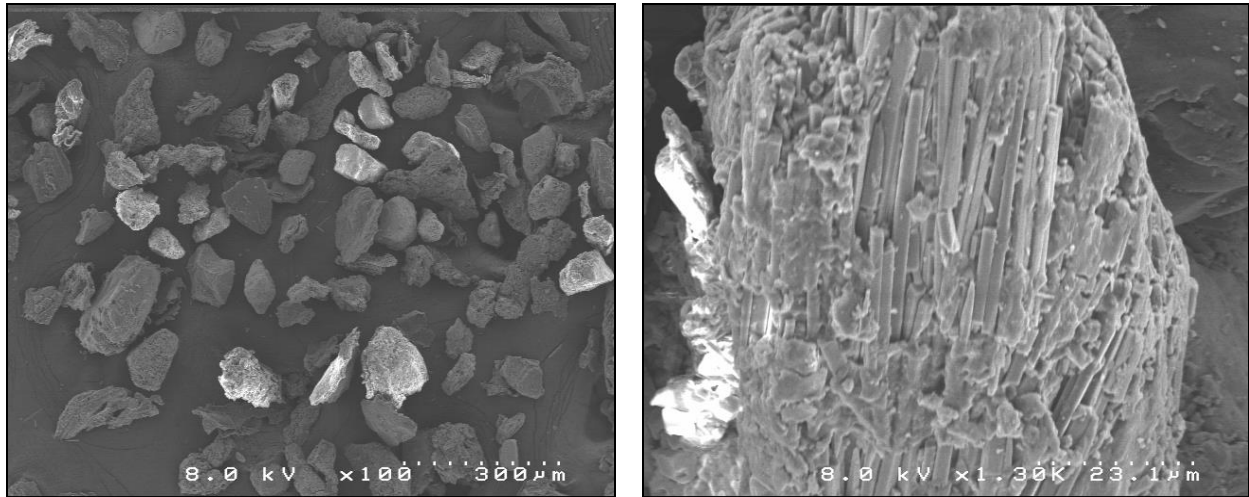


Figure 1 : Scanning electron micrograph of *C. edulis* particles (< 500 μm).

Scanning electron microscopic photographs of *C. edulis* particles shown in figure 1 reveal the surface texture and porosity of the sample. SEM images of micro-particles of dry *C. edulis* plant indicate the presence of grains and organic fibres in the structure. The morphology of this material can facilitate the adsorption of metals, due to the irregular surface of the *C. edulis* particles, thus makes possible the adsorption of metals in different parts of this material. So, based on the morphology, as well as on the fact that high amounts of amino acid and tannins [Chiban (2007a)], it can be concluded that this material presents an adequate morphological profile to retain metal ions. The qualitative EDX spectra for micro-particles of dry *C. edulis* plant (figure 2) indicated that Oxygen, Carbon, Calcium, Silicon, Sulphur, Aluminium, sodium, and Manganese are the main constituents. These had been known as the principal elements of *C. edulis* particles.

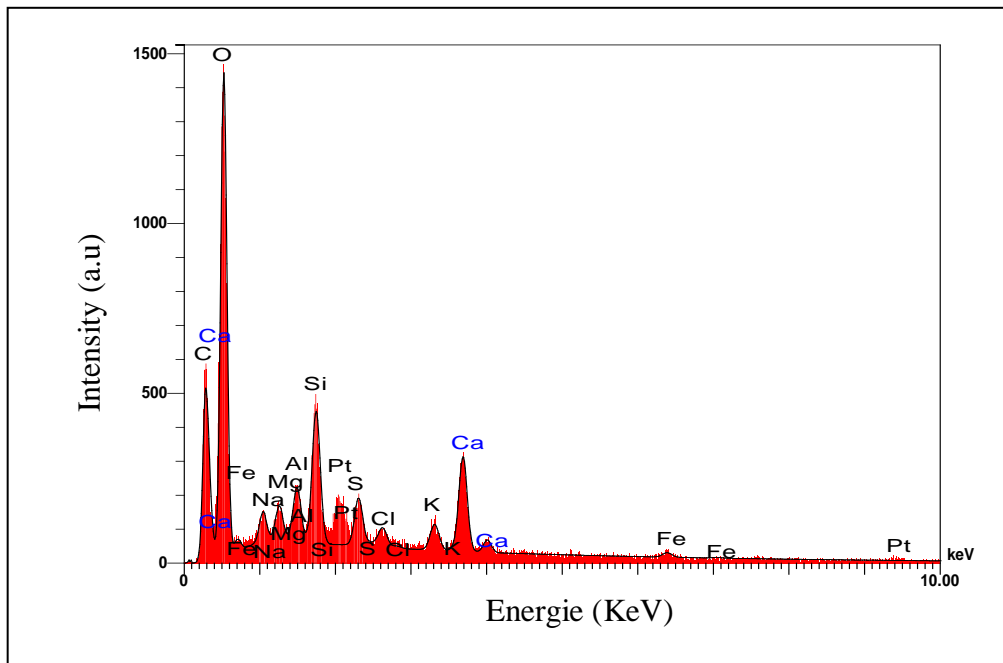


Figure 2 : EDX spectrum of *C. edulis* particles (< 500 μm).

1. Composition wastewater samples

Two different types wastewater were studied. Anza and M'Zar wastewater samples are industrial and domestic wastewater of Agadir zones (in south-western Morocco). The composition of real wastewater samples is shown in table 1.

Table 1: Composition of domestic and industrial wastewaters.

	M'Zar wastewater (mg/l)	Anza wastewater (mg/l)	N_{EVMA} [AFNOR (1994)] (mg/l)
Pb²⁺	0.40	6.093	0.050
Cd²⁺	0	0.068	0.005
Cu²⁺	0.75	2.131	1
Zn²⁺	1.13	17.351	5
NO₃⁻	123.5	2.976	50
PO₄³⁻	98.5	81.58	0.05
DCO	1274	1575.33	30
MES	1023	1034.33	25
pH	7.67	2.23	6.5<pH<9.5
T (°C)	24	24.33	< 25

EUA: Average concentration of pollutants of Anza wastewater (mg/l) for several samples.

EUM: concentration of pollutants of M'Zar wastewater samples (mg/l)

N_{EDW}: European norms in drinking water (mg/l)

These results indicate that M'zar wastewater contain a low concentration of heavy metals but high concentration of pollutant minerals, including NO₃⁻, PO₄³⁻. It shows also the high COD (The Chemical Oxygen Demand) values. The value obtained for nitrates and phosphates ions are superior to ward the European norms. From these values, we note that the Anza wastewater samples contain higher concentrations of heavy metals than the M'zar wastewater samples.

The adsorption studies of all pollutants from wastewater onto *C. edulis* adsorbent are studied using the average concentration of these pollutants from several wastewater samples. The values of pH and Temperature of M'zar wastewater samples are 7.67 and 24°C respectively. These values don't present a danger for flora and fauna.

2. Nitrates and orthophosphates adsorption from real wastewater

The variations of the concentrations of nitrates and orthophosphates ions retained from domestic and industrial wastewaters selected versus the contact time are plotted in figures 3 and 4 for *C. edulis* plant as adsorbent.

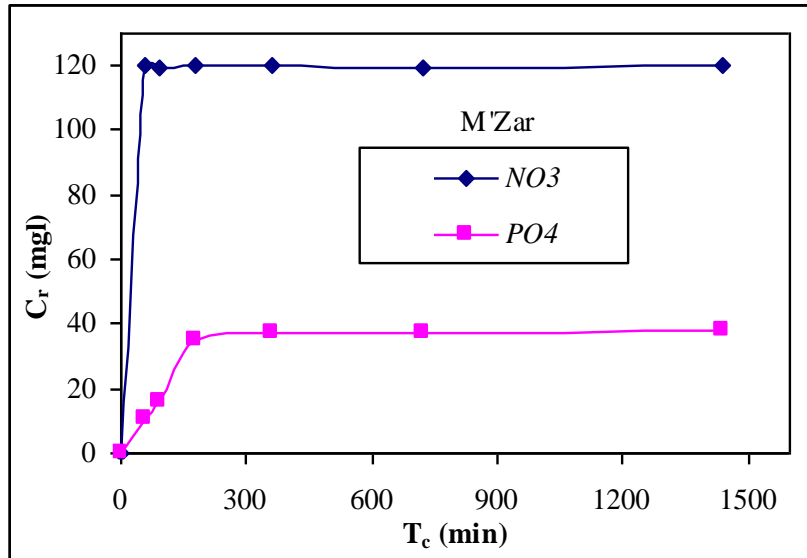


Figure 3 : Adsorption of NO_3^- and PO_4^{3-} ions from M'Zar wastewater by one gram of *C. edulis* plant: $C_0(NO_3^-) = 123.5$ mg/l, $C_0(PO_4^{3-}) = 98.5$ mg/l, $m/v = 25$ g/l.

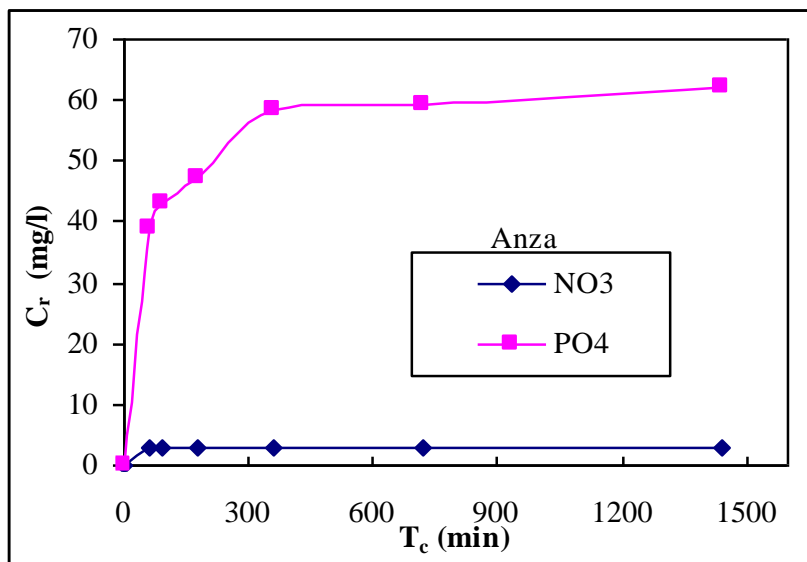


Figure 4 : Adsorption of NO_3^- and PO_4^{3-} ions from Anza wastewater by one gram of *C. edulis* plant : $C_0(NO_3^-) = 2.97$ mg/l, $C_0(PO_4^{3-}) = 81.58$ mg/l, $m/v = 25$ g/l.

From these results, we note that the adsorbent using micro-particles of *C. edulis* plant present a good retention of nitrate ions. This retention increased with an increase of contact time. The process of orthophosphates ions uptake by the *C. edulis* appeared to follow a two phase process characterised by an initial fast retention step lasting at the maximum less than 30 minutes, and corresponding to an uptake concentration of about 73 to 77 % of the initial PO_4^{3-} concentration of the Anza wastewater, followed by a much slower step lasting for hours and tending to a steady state. Equilibrium is attained in less than 6 hours. Nitrates, shows rapid adsorption kinetics with up to 98 % nitrate ion removal in the first 30 minutes. After the fast initial process, the adsorption proceeds at a slower rate, before reaching a plateau. The final nitrate ions concentrations ($C_f < 3$ mg/l) are much lower than 25 mg/l, which is the norm of drinking water [AFNOR (1994)].

Under these experimental conditions the maximum efficiency for nitrates and orthophosphates ions uptake by unit of weight of plant is higher than 4.8 mg/g. These values depend on the type of anions as the uptake of NO_3^- is higher than that for PO_4^{3-} , indicating some specificity of the interactions between the nitrate and orthophosphates anions and the sites of the *C. edulis* plant responsible for the ion uptake. These results are much lower in comparison with those obtained for laboratory solution. The concentrations retained by *C. edulis* of nitrate and orthophosphates ions from aqueous solution are 3 g/l for NO_3^- and 0.62 g/l for PO_4^{3-} respectively [Chiban (2006)].

These experiments confirm the efficiency of the adsorbent issued from dried *C. edulis* plant of the southern Morocco to retain water soluble nitrate and phosphate anions. The very fast adsorption kinetics, observed for *C. edulis* plant, represents a key advantage for designing water treatment systems based on this principle.

The results of adsorption onto micro-particles of *C. edulis* plant with the distilled water shows that the negligible quantities of nitrate and phosphate ions are release by these micro-particles of *C. edulis* plant ($Q_{\text{rel}}(\text{NO}_3^-) < 0.01 \text{ mg/g}$, after 24 hours of contact time).

3. Heavy metals adsorption and chemical oxygen demand from domestic and industrial wastewater samples

The M'Zar wastewater samples contain a low concentration of heavy metals including Cu(II), Cd(II), Pb(II) and Zn(II). It is not necessary to study the adsorption process at different contact time. The adsorption of heavy metals by micro-particles of dry plant after 3 hours of contact time has been studied. The results show that the adsorption capacity of *C. edulis* plant was found to be 0.025 mg/g for Cu(II), 0.016 mg/g for Pb(II) and 0.034 mg/g for Zn(II). These experimental results of the adsorption process on new adsorbent obtained from *C. edulis* plant showed that these adsorbents have greed capacity to remove heavy metals ions from real wastewater.

The variations of the concentrations of heavy metals ions adsorbed by micro-particles of dry *C. edulis* plant from Anza wastewaters versus the contact time are plotted in Figure 5.

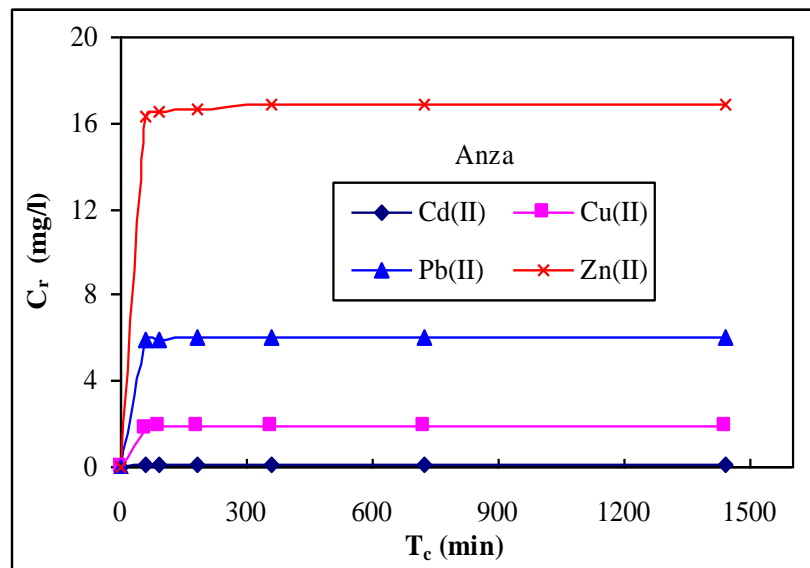


Figure 5 : Adsorption of heavy metals from Anza wastewater by one gram of *C. edulis* plant : C_0 (Cd) = 0.068 mg/l, C_0 (Cu) = 2.131 mg/l, C_0 (Pb) = 6.093 mg/l, C_0 (Zn) = 17.351 mg/l, $m/v=25 \text{ g/l}$.

The results of heavy metals adsorption from Anza wastewater indicates that : i) The adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) ions by *C. edulis* plant are about 77.22, 2.50, 243.37 and 676.43 $\mu\text{g/g}$ respectively and ii) the treated wastewater onto micro-particles of dried *C. edulis* plant fulfills the requirements of World Health Organisation (WHO, 1971). The removal percentage of heavy metals by *C. edulis* was 94% for Cd(II), 91% for Cu(II), 99% for Pb(II) and 98% for Zn(II). These values are much lower in comparison with those obtained for laboratory solution at various concentrations, i.e. the concentrations adsorbed by these biomaterials of heavy metal from laboratory solution are 4.375 g/l, 0.7 g/l, 1.13 and 0.96 for lead, cadmium, copper and zinc respectively [Chiban (2006)]. A similar trend has been observed in the removal of divalent metal ions (Cu(II), Cd(II), Zn(II) and Pb(II)) by 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 and Salim (2002, 1994)].

4. Chemical oxygen demand (COD)

The effect of contact time under agitation on the supplement COD from M'Zar and Anza wastewaters by *C. edulis* particles is illustrated in figure 6.

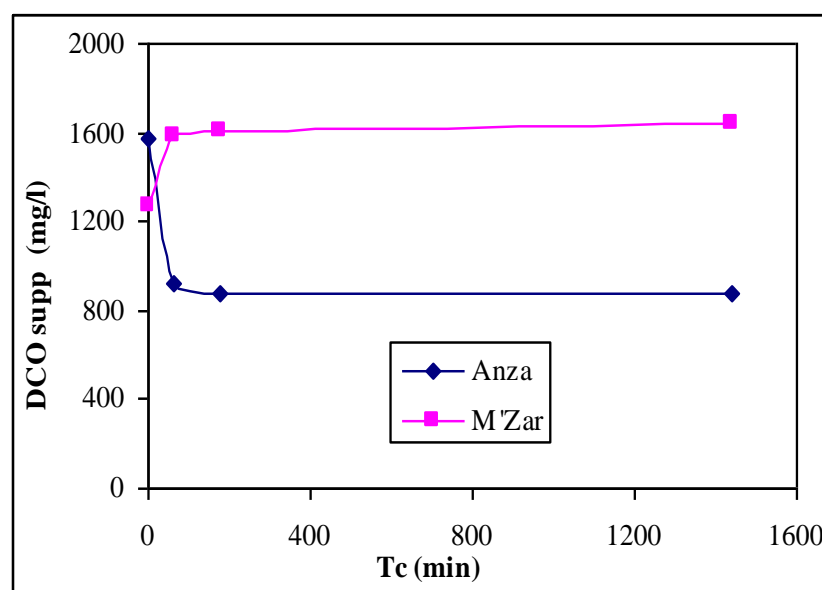


Figure 6 : Effect of contact time variation of the COD supplement by gram of *C. edulis* plant :
 $T=25^{\circ}\text{C}$, $m/v=25\text{g/l}$ and natural pH.

In the case M'zar wastewater, the results indicate that the release of organic matter in solution by adsorbent issued from *C. edulis* increased with an increase of contact time. But for Anza wastewater samples, these results show that the COD supplement decrease with contact time. This can be explained by the different in pH of wastewater samples ($\text{pH}(\text{Anza}) = 2.23$, $\text{pH}(\text{M'Zar}) = 7.67$).

The tests of adsorption process with the distilled water also showed that the *C. edulis* plant can release the amounts important in solution of organic matter, what suggests the necessity of a pre-wash before use of the these micro-particles of dried *C. edulis* plant [Chiban (2007b)].

CONCLUSION

This study indicated that the micro-particles issued from grinded and dried *Carpobrotus edulis* plant could be used as adsorbents for the treatment of wastewater contaminated with heavy metals and pollutant minerals such as ; nitrate and phosphate. The maximum removal of nitrates and phosphates ions from M'Zar wastewater samples was found to be 98% and 41% at pH 7.67 and temperature ambient for *C. edulis* plant, respectively. The removal percentage of heavy metals from Anza wastewater onto *C. edulis* plant was about to 94% for Cd(II), 91% for Cu(II), 99% for Pb(II) and 98% for Zn(II). The adsorption process of heavy metals, nitrates and orthophosphates by the different biomaterials was affected by various parameters such as pH values, contact time and initial ions concentrations in solution. The maximum capacity adsorption was depending on the type of ions.

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