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Full Length Research Paper

Use of Mediterranean plant as potential adsorbent for municipal and industrial wastewater treatment

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A batch adsorption system using dried *Carpobrotus edulis* plant as a new cheap adsorbent was investigated to remove some pollutants from raw wastewater. The results show that the uptake of nitrate, phosphate and some heavy metals ions from wastewater by *C. edulis* increased with increasing contact time. The percentage uptake of heavy metals from industrial wastewater by *C. edulis* particles was about ~94% for Cd(II), ~91% for Cu(II), ~99% for Pb(II) and ~98% for Zn(II). The removal percentage of phosphate and nitrate ions from municipal wastewaters by dried *C. edulis* was found to be ~96 and ~97%, respectively. The results indicate that the chemical oxygen demand values decreased after contact with micro-particles of dried *C. edulis* plant. The maximum uptake capacity was depending on the type of wastewater as well as the type of pollutant.

Key words: Dried *Carpobrotus edulis* plant, wastewater treatment, phosphate, nitrate, heavy metals.

INTRODUCTION

Municipal and industrial wastewaters frequently contain phosphate, nitrate and heavy metals ions. The industrial use of metals increases their concentrations in soil, air and water. The trace metals are widely spread in environment and may enter the food chain from the environment. It is well recognized that the presence of metals ions in the environment can be detrimental to a variety of living species (Benhima et al., 2008). Unlike organic pollutants, metals are non-biodegradable and because of this the removal of heavy metals becomes essential. Also, nitrate and phosphate ions are commonly found in various wastewaters. They can cause serious water pollution and threaten the environment (Barber and Stuckey, 2000). It is therefore, essential to control and prevent their unsystematic discharge in the environment. For this reason, increased attention is being focussed on the development of technical know how for their removal from nitrate, phosphate and metal bearing effluents before being discharged into water bodies and natural streams.

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The conventional methods used to remove toxic cations and anions from wastewaters are membrane techniques (reverse osmosis, nanofiltration, etc.), oxidation/p recipitation (hydroxides, sulfides, etc.), coagulation and flocculation, ion-exchange, adsorption by activated carbon (Zhao and Sengupta, 1998; Babel and Kurniawan, 2003; Igwe and Abia, 2003; Ozturk and Bektas, 2004; Mohan and Pittman Jr, 2007) etc.

However, these methods have certain disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal (Özcan et al., 2005). The adsorption process is one of the most efficient methods of removing pollutants from wastewaters. It is the process that is used to collect soluble substances in solution on a suitable interface. The ability of adsorption to remove toxic chemicals without disturbing the quality of waters or leaving behind any toxic degraded products has augmented its usage in comparison to electro-chemical, biochemical or photochemical degradation processes (Mittal, 2006). Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Namasivayam et al., 2001). There are large numbers of studies in the literature in which various adsorbents are used. Two recent reviews reported by (Mohan and Pitman, 2006; Kurniawan et al., 2006) can be referred for the other possible adsorbents for the removal of heavy metals. However, the adsorption capacity of the adsorbents is not very large. For the past few years, the focus of the research is to use cheap materials as potential adsorbents and the processes developed so far are based on exploring those natural adsorbent, which can prove economic and bring cost effectiveness (Benhima et al., 2008; Chiban et al., 2011).

The use of dried plants in the wastewaters treatment has been studied in recent years and the results of the laboratory investigations showed that dried plants are good adsorbents for the removal of arsenate, nitrate, phosphate, cadmium and lead ions from synthetic wastewaters (Benhima et al., 2008; Abdel-Halim et al., 2003; Chiban et al., 2005, 2009, 2011). In this study, the plant selected to be used as an environmentally friendly adsorbent of phosphate, nitrate and heavy metals ions from municipal and industrial wastewater samples was *C. edulis* plant from the Mediterranean area of Morocco. *Carpobrotus edulis* is a plant from the Aizoaceae family, the stems are spread over 2 m long, the leaves 4 to 8 mm long, 8 to 17 mm in width and color-bright green. The flowers are 10 to 20 mm in length. This plant has an effective antibacterial activity (Vander-Watt and Pretorius, 2001). The objective of our work was to investigate the possible use of a new cheap adsorbent obtained from the dried *C. edulis* plant as an alternate material for wastewater treatment using the batch equilibration technique.

MATERIALS AND METHODS

The material used in this study was obtained from *Carpobrotus edulis* plant as previously reported (Benhima et al., 2008; Chiban et al., 2011). A recent screening (Chiban et al., 2007) of the chemical composition and surface characterization of the plant points out that the major functional groups on *C. edulis* plant are polar hydroxyl, aldehydic and carboxylic groups. Due to this *C. edulis* has a great potential as adsorbent of anions and cations from aqueous solutions. The plant parts (leaves and stems) were dried under air during one week. The dried plants were chopped into small fragments, then again dried in oven at 35°C during 24 h and crushed with an electric grinder to get fine powders. The obtained micro-particles were used as adsorbent materials in batch experiments without any other pre-treatment to avoid extra costs.

Several raw wastewater samples were collected from two Agadir zones (Drarga and Anza regions) and stored in polyethylene bottles. Drarga and Anza wastewater samples are municipal and industrial wastewaters from Agadir zones, respectively. These samples were decanted and filtered on paper of 0.45 µm porosity. The pollutant charge of wastewater samples has been determined before using them for the batch experiments.

Batch experiments

The removal of pollutants from wastewaters was performed by batch technique at room temperature. About 1 g of dried *C. edulis* plant was accurately weighed and placed in Erlenmeyer glass flasks of 100 ml containing 40 ml of wastewater solution of known concentration and pH. The solutions were vigorously stirred by use of a magnetic stirrer at a constant temperature for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After different contact times (Tc), were centrifuged at 5000 rpm for 10 min and the supernatant was filtered. The concentrations of nitrate and phosphate ions of the filtrates were measured by Waters model capillary electrophoreses and HP model spectrophotometer, respectively.

The chemical oxygen demand (COD) was measured using HACH 8000 spectrophotometer and the total suspended solids (TSS) was determined by weighing filtered (Whatman filter paper of 0.45 µm) samples after drying for 24 h at 105°C. The instrument used for the determination of lead, cadmium, copper and zinc ions concentration was a Varian model 220FS atomic absorption spectrophotometer. The pH values of the wastewater samples were measured by a Mettler-Toledo meter (MP120) with a glass electrode. A mechanical shaker model Labotec was used for shaking the adsorption batches. The centrifuge Biofuge model (Heraeus Instruments) was used to separate dried plants from the solutions after complete adsorption experiments. An analytical balance Precisa model XT 220A was used for weighting the dried plants samples.

The pollutant concentration retained in the adsorbent phase (q_a, mg/g) and percentage uptakes (%) were calculated by the equations:

$$q_a = (C_i - C_t) \times \frac{V}{m}$$

$$\%\ \text{uptake} = \left[\frac{C_i - C_t}{C_i}\right] \times 100,$$

where C_i (mg/l) is the initial concentration of pollutant in the feed solution, C_t (mg/l) is the concentration of pollutant in solution at a given time't', V (ml) is the total volume of the feed solution; and m (g) is the weight of the material.

RESULTS AND DISCUSSION

The composition of wastewater samples is shown in Table 1. These results show that the raw wastewater samples are richer in heavy metals and phosphate and they also show the high COD (Chemical Oxygen Demand) and TSS (Total Suspended Solids) values. All the values obtained for pollutants, except nitrate ions, are superior to Moroccan norms and World Health Organization standard for drinking water (Standard, 1991; WHO, 2008). The average pH and temperature values of raw industrial wastewaters are 2.2 and ~24°C, respectively. These values show that the industrial wastewater samples are very acid.

These results indicate that municipal wastewater contain a low concentration of cations but high concentration of anions. It shows also the high values of COD (Chemical Oxygen Demand) and TSS (Total Suspended Solids). While, the industrial wastewater samples contain high heavy metals and phosphate concentration but low nitrate ions concentration. The average pH and temperature values of municipal and industrial

Table 1. Composition of municipal and industrial wastewater samples.

Pollutant	Unit	Municipal wastewater*	Industrial wastewater*	WHO standard for drinking water (WHO, 2008)
Pb^{2+}	mg/l	0.124	6.093	0.05
Cd^{2+}	mg/l	0.16×10^{-4}	0.068	0.005
Cu^{2+}	mg/l	0.185	2.131	1
Zn^{2+}	mg/l	0.32	17.35	5
NO_3^-	mg/l	92.9	2.976	50
PO_4^{3-}	mg/l	62.3	81.58	0.05
COD	mg O_2/l	1046	1575	30
TSS	mg/l	602	1034	25
pH	-	8.1	2.2	6.5<pH<9.5
T	°C	23	24	< 25

*: Indicate average pollutants concentration for several samples (mg/l).

wastewaters are 8.1, 2.2 and ~23, ~24°C, respectively. These values show that the industrial wastewater samples are very acid then municipal wastewaters. The variations of the residual concentration and % removal of both phosphate and nitrate ions from municipal and industrial wastewater samples versus the contact time are plotted in Figure 1. Based on previous work, the m/V ratio was chosen to 25 g/l (1g/40 ml) for this study in all batch experiments. A detailed study for determining the ratio of the weight of *C. edulis* adsorbent to volume of the aqueous phase (*m/V*) has been done by laboratory solution as it was described in our previous report (Benhima et al., 2008).

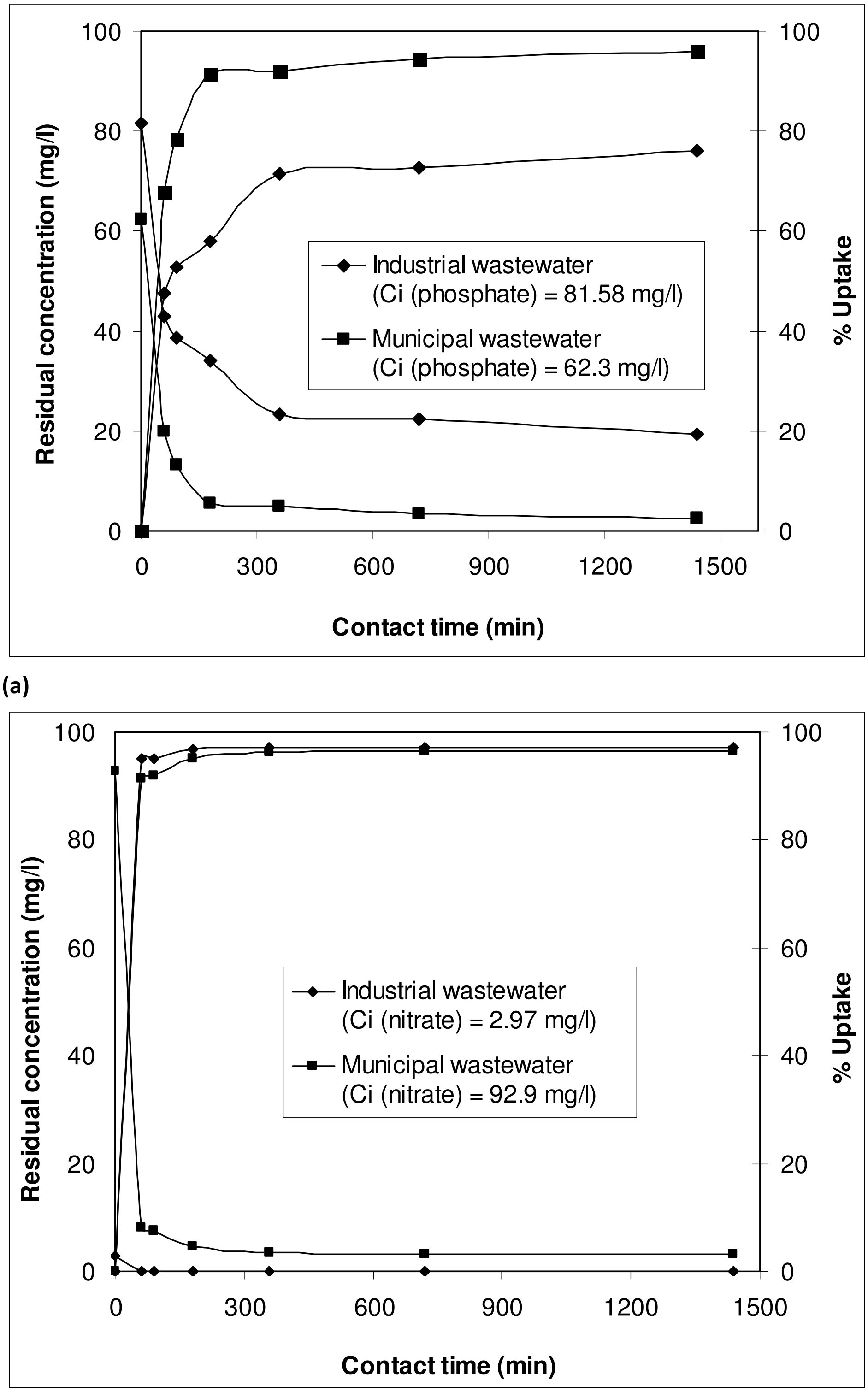
From these results, we note that the residual concentration of phosphate and nitrate ions in solution decreased with the increasing of the contact time. So, the % uptake of *C. edulis* particles increased with the increasing of the contact time. The adsorption process of both anions uptake by dried *C. edulis* plant appeared to follow a process in two phases characterized by an initial fast uptake step lasting at the maximum, less than 1 h, and corresponding to an uptake concentration of about ~53 to 77% and ~95 to 98% of the initial PO_4^{3-} and NO_3^- concentration ions of the both wastewater samples, followed by a slower step lasting for hours and tending to a steady state. The equilibrium time is attained in less than 3 hours for phosphate and 1 h for nitrate ions. This difference can be explained by the type of wastewater. The final nitrate ions concentrations are lower than 25 mg/l, which is the norm of drinking water. The maximum uptake capacities of phosphate and nitrate ions by unit of weight of dried plant were 2.40, 3.59 mg/g respectively. These values depend on the type of anions because the uptake of NO_3^- is higher than that for PO_4^{3-} ions.

This indicates some specificity of the interactions between anions and active sites of dried *C. edulis* plant responsible for the anions adsorption. The results of nitrate and phosphate ions uptake onto *C. edulis* with distilled water show that the negligible quantities of these elements are release into solution by these micro-particles.

As shown in Tabe 1, the municipal wastewater samples contain a low concentrations of heavy metals including Cu(II), Cd(II) and Zn(II) comparing to the European norms. For this reason, it is not necessary to study the removal of these elements at different contact time. The variations of the residual concentration and the removal percentage of Pb(II) ions by dried *C. edulis* plant from municipal wastewaters versus the contact time are presented in Figure 2. These results show that the maximum uptake capacity of Pb(II) ions at equilibrium was found to be 3.36×10^{-3} mg/g. The percentage removal of Pb(II) ions from municipal wastewaters by dried plant was noticed at about 64% after 30 min of contact time. In the case of industrial wastewaters, the variations of the percentage removal of heavy metals ions by *C. edulis* micro-particles versus the contact time are plotted in Figure 3. These results show that the removal of heavy metals ions was very fast and the equilibrium was reached within 60 min. Equilibrium sorption efficiency for Pb(II) was achieved ~98 to 99% with an initial solution concentration of 6.09 mg/l. About 90% of the equilibrium Pb(II) uptake was removed rapidly within first 15 minutes. This indicates a high sorption rate for heavy metals ions from real wastewaters. It is also noticed that:

1. The uptake quantities of Cu(II), Cd(II), Pb(II) and Zn(II) ions by *C. edulis* particles are about 77.18, 2.53, 243.26 and 676.40 µg/g respectively and,
2. The percentage removed of heavy metals by *C. edulis* plant was found to be ~99% for Pb(II), ~93% for Cd(II), ~90% for Cu(II) and ~97% for Zn(II),
3. The treated wastewater on dried *C. edulis* plant fulfils the requirements of WHO (WHO, 2008).

It is clear that the maximum % removed was depending on the type of the metal ions. These values are much lower comparing to those obtained for laboratory



(b)

Figure 1. Residual concentration and % uptake of phosphate and nitrate from municipal and industrial wastewaters using *C. edulis:* (a) = phosphate ions; (b) = nitrate ions.

solutions at various concentrations (Benhima et al., 2008). In the studied conditions, the % removal of metal ions from industrial wastewater samples followed the order of Pb(II) > Cd(II) > Zn(II) > Cu(II).

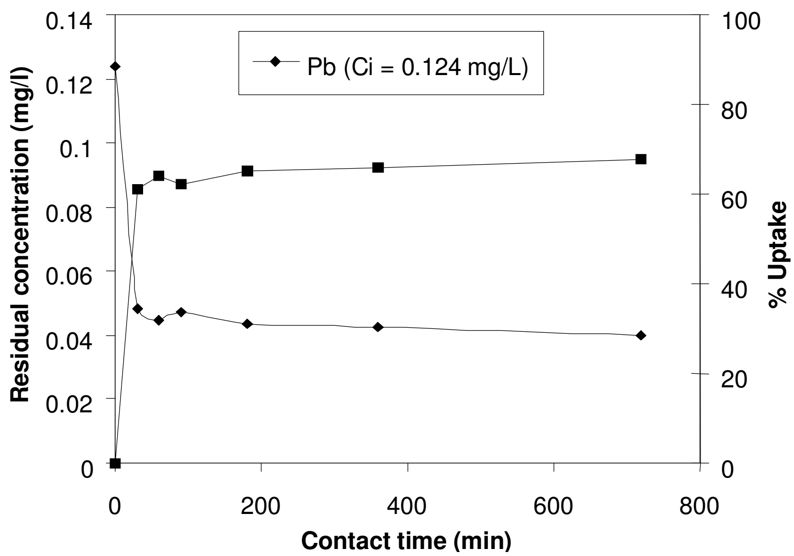


Figure 2. Residual concentration and uptake of Pb(II) ions from municipal wastewater by dried *C. edulis* plant : C_i (Pb)=0.124 mg/l, *m/V*=25 g/l, pH=8.1, T=23°C.

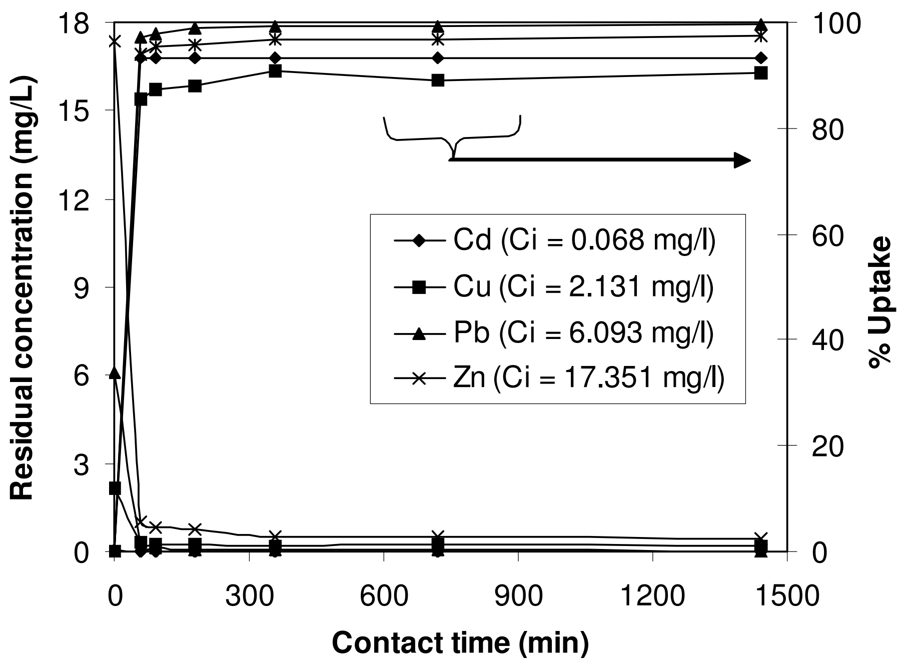


Figure 3. Residual concentration and uptake of heavy metals from industrial wastewater by dried *C. edulis* plant : C_i (Cd)=0.068 mg/l, C_i (Cu)=2.13 mg/l, C_i (Pb)=6.09 mg/l, Ci (Zn)=17.35 mg/l, pH=2.2, T=24°C.

In order to evaluate any release of heavy metals ions by these micro-particles, the same amount of *C. edulis* plant was mixed with pure water. Released amounts of these ions in the order of 1.0×10^{-3} mg/l for Cd(II), 1.9×10^{-3} mg/l for Pb(II), 4.2×10^{-2} mg/l for Cu(II), 6.5×10^{-2} mg/l for Zn(II) have been measured after 12 h of contact with dried *C. edulis* plant. These values are negligible.

The effect of contact time under agitation on the supplement COD from municipal and industrial wastewaters by *C. edulis* particles is illustrated in Figure 4. As shown in Figure 4, the release of organic matter in

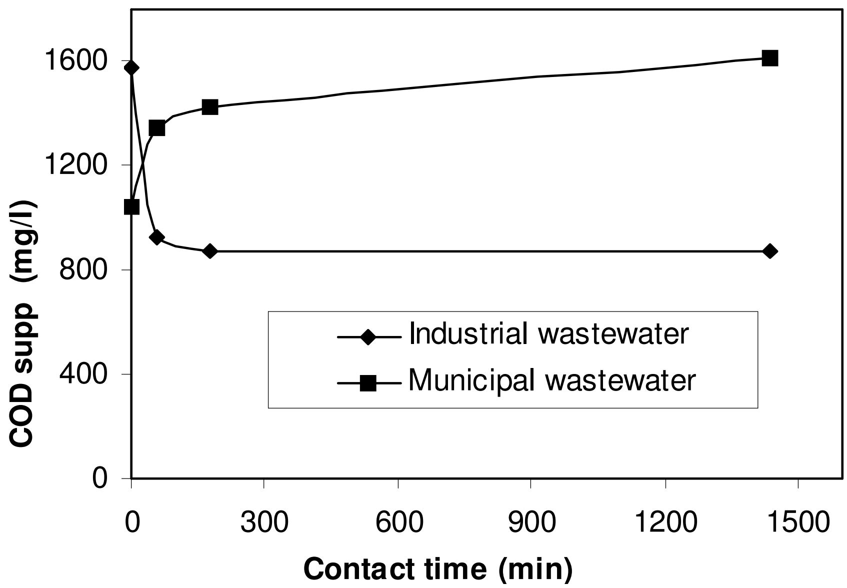


Figure 4. Effect of contact time on the COD supplement: T=25°C, *m/V*=25g/l and natural pH.

municipal wastewater samples by dried *C. edulis* increased with increasing of the contact time. In the case of industrial wastewater samples, these results show that the COD supplement decrease with contact time. This difference can be explained by the variation of the pH of wastewater samples (pH_{ind}=2.2, pH_{mun}=8.1). The tests of adsorption process with distilled water showed that the dried *C. edulis* plant can release important amounts of organic matter in solution, which suggests the necessity of a pre-wash before using these micro-particles of dried *C. edulis* plant.

The experimental results of this study can be used to design batch adsorption systems for the nitrate, phosphate and heavy metals ions removal. Such a batch system will be applicable to small industries which generate heavy metals-containing wastewaters. The adsorbent can be added to the wastewater collected in a tank and the mixture must be agitated for the equilibrium time found from this study. Then the liquid can be decanted and discharged. Because of low pH, the adjustment of pH is necessary before discharging to a sewer or water course. The used adsorbent has to be suitably disposed.

Conclusion

This study indicated that the dried *Carpobrotus edulis* plant could be used as an environmentally friendly material for municipal and industrial wastewater treatment. The maximum uptake percentage of *C. edulis* plant was found to be ~98% for NO_3^-, ~41% for PO_4^{3-}, ~94% for Cd(II), ~91% for Cu(II), ~99% for Pb(II) and ~98% for Zn(II). The maximum uptake capacities were depending on the type of pollutant as well as on the type of wastewater.

The method presented in this work might be of interest for industrial and environmental applications for the removal of toxic metal ions from the environmental. Using dried plants for the removal of pollutants have the advantages of being available, cheap and efficient. The contaminated dried plants are expected to precipitate and became a part of the sediment. However, using this method for treatment of industrial effluents might require finding a way for a proper disposal of the dried plants.

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