RIGINAL ARTICLE

A COMPARISON BETWEEN NORMAL, SIMULTANEOUS AND SUCCESSIVE ADSORPTIONOF NITRATE AND ORTHOPHOSPHATE IONS BY BIOMATERIALS

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ABSTRACT

We were interested to the comparative study of normal, simultaneous and successive adsorption of nitrates and orthophosphates ions on the inert solid biomaterials (ISBM) obtained from dried of plants of *Carpobrotus edulis*(*CE*).
Adsorption is called simultaneous (binary component systems) when it is obtained from a solution which contains nitrates and orthophosphates ions. The adsorption is called successive when we used the ISBM which has already used in another adsorption to equilibrium saturation. The efficiency of this ISBM was investigated using batch adsorption technique under different experiment conditions. These results showed that the adsorption of $NO_3^-$and HPO_4^{2-} ions from single and binary component systems are identical, This absence of competition between these ions on the sites of adsorption can be explained by their adsorption on different sites .The structure very different from the two mineral anions is in favour of this suggestion
Key words: *inert solid biomaterials, Nitrates, Orthophosphates, Adsorption.*

1. INTRODUCTION

Pollution of ground and surface waters by nitrates and phosphates is a wide spread and serious problem. Several nitrogenous compounds, including orthophosphates and nitrate have been frequently present in drinking water and various types of agricultural, domestic and industrial wastewater [1,2]. Nitrate and phosphates 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 liked outbreaks of infectious disease [3]. Excess nitrate in drinking water may methemoglobinaemia also called a blue baby disease, in newborn infants [4, 5].

Various techniques have been used for nitrate and orthophosphate removal. It's fall into three main categories: physical, chemical and biological. The physical methods proved to be either too expensive, as in the case of electrodialysis and of reverse osmosis [6], or inefficient, removing only 10% of the total phosphorus [7]. An enhanced biological treatment can remove up to 97% of the total phosphorus, but this process can be highly variable due to the operational difficulties [7]. The chemical treatment is widelyused for the removal of nitrate and orthophosphate ions. Theadsorption is one of the techniques which would be more usefuland economic for this aim. In the recent years, has been widelyinvestigated the application of the low-cost and easily availablematerials in wastewaters treatment [8] and a considerable attention has been devoted to the study of different types of low-costmaterials such as tree bark, wood charcoal, saw dust, alum sludge,red mud and other waste materials for the adsorption of some toxicsubstances [9,10,11].

The process described in this work is simple, cheap and easy to extrapolate at a larger scale for a practical application to the treament of wastewaters. It consists in the use of the micro-particles obtained from dried *Carpobrotus edulis* plant which are brought in contact with the anions and heavy metals solutions. The adsorption by these micro-particles of the dried plant might be attributed mainly to their protein, carbohydrates and phenolic compounds [12], which contain anion-binding functional groups as carboxyl, hydroxyl, sulfate, phosphate and amino groups [11,12,13,14].

In this study we want to analyze the removal of NO_3^- and HPO_4^{2-} from single and binary component systems onto the dried *Carpobrotus edulis* plant.

2. 2. Materials and methods

3. 2.1. Materials, chemicals and equipment

*C. edulis*plant was collected from the region of Agadir (Mediterranean zone of Morocco). The dried stems and leaves of*C. edulis*plant were converted into micro-particles by grinding them in amechanical grinder. These micro-particles of*C. edulis*plant wereused as adsorbent materials. They are known to have a richpolypeptides content, the importance of which has been demon-strated in previous work, regarding the ion binding [15]. Thesepolypeptides and other

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biomolecules (Alkaloids, Terpenes, Phenolic compounds, Saponines ...) would contain the responsible sites forthe ionic adsorption, such as functional groups: –COOH, –NH, –OH [13, 14-16, 17, 18]. The surface area of*C. edulis*particles was measuredby BET method at 77 K using ASAP 2010 Micrometrics (EuropeanMembrane Institute, Montpellier, France). The photomicrographyof the exterior surface of*C.edulis*particles was obtained by scanningelectronic microscopy (SEM, HITACHI S-4500). The distribution ofthe elemental concentrations for the solid sample can be analyzedusing the mapping analysis of SEM/EDX (EDX, LEICA-S-260. Thesurface area ofC. edulisparticles was defined as 2.6 m^2/g. All chemicals used in this study were of analytical grade reagents from Fluka.

2.2. Batch adsorption studies

In the batch adsorption experiments, 40 mL of aC_i concentration solution was mixed with 1g of dried plant without anypre-treatment, the mixture being vigorously stirred with the use ofa magnetic stirrer. The solution with the dried plant material wasmaintained in water bath thermostat, at a constant temperature.

The time needed to reach the adsorption equilibrium for an initialgiven ions concentration was determined by sampling aliquots ofsolution analyzed during 24 h periods. The sampled solutions werecentrifugated at 5000 rpm for 15 min with a Biofuge model centrifugation machine from Heraeus Instruments.

2.3. Preparation of adsorption media

Individual HPO_4^{2-} and NO_3^-solutions were prepared by dissolving a known amount of Na_2HPO_4, $12H_2O$ and KNO_3salts in bidistilled water. Theconcentration of the prepared ions solution = 100mg/l(at low concentrations) for both anions, this solutions =3.5g/l for HPO_4^{2-} and 4.5g/l for NO_3^- (at high concentrations). Before mixing them with theplant suspension.

2.4 Analysis and calculation of the adsorbed quantities Method

The technique used for the dosage of these ions is according to spectrophotometric method AFNOR norm. The spectrophotometer used as a scanning spectrophotometer Jenway 6405 category.

The retained concentrations Cr (mg / l) by the biomaterial at the equilibrium and quantity of adsorption Qads (mg / g) are given by the following relationships:

$$C_r(mg/l) = Ci - C_{eq}$$

$$Q_{ads}(mg/g) = (Ci - C_{eq})x\frac{V}{m}$$

M:Mass of crushed CCB in(g),
V: Total volum in (l),
Ci: initial concentration in (mg/l),
Ce: Equilibrium concentration in (mg/l),
Q_{ads}: Adsorbed quantity per 1gram of BMIS in (mg/g).

4. 3. RESULTS AND DISCUSSION

5. 3.1. Characterization of Carpobrotus edulis plant

6. 3.1.1. Morphology of C. edulis micro-particles

SEM is widely used to study the morphological features of the particles. SEM photographs of *C. edulis* microparticles (Figure1) indicate the presence of grains and organic fibres in the structure**.** We can also observe the pores in structure.

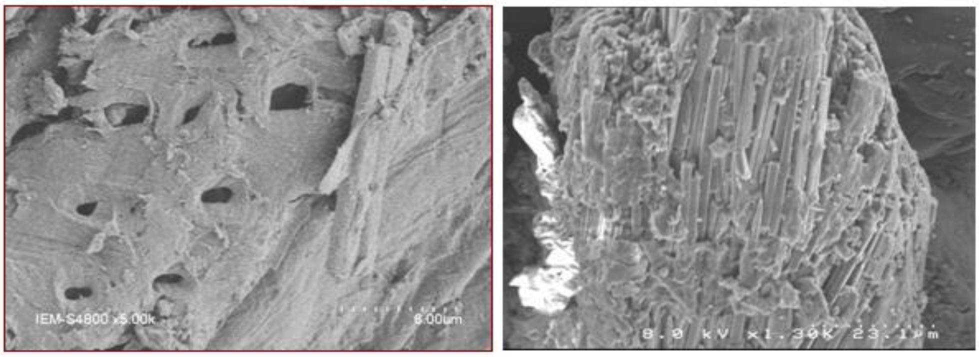

Figure1: SEM of *C. edulis* particules.

3.1.2. Atomic composition of *C. edulis*

EDX spectrum (Figure2) shows the presence of O, C, Ca, Si, S, Al, Na and Mg in the dried *C. edulis*. The chemical composition of *C. edulis* plant is: 5.27% Ca, 4.00% Si, 29.05% C and 52.48% O. These have been known as the principal elements of *C. edulis* particles.

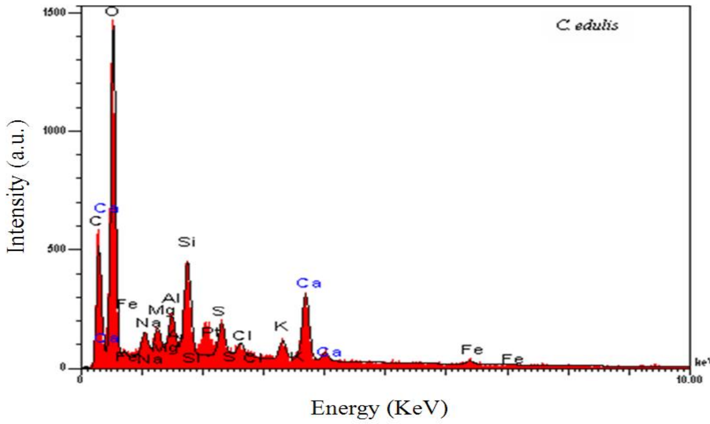

Figure2: EDX spectrum of *C. edulis* particles.

3.1.3. IR spectrum of *C. edulis*

The results of IR are quite helpful in the identification of various forms of minerals present in the biomaterial. The IR of *C. edulis* plant used in this study is presented in Figure3. This spectrum presents typical absorption bands found in the IR spectrum of the biomolecules (Figure4) [19]. IR spectra of these biomolecules shows absorption band at 3300 cm^{-1} of corresponding to hydroxyls (OH) and amines (NH) groups, the broad peak at 2900 cm^{-1} can be attributed to the vibration absorption band of –CH group. The peak located at 1600 cm^{-1} is a characteristic of carboxyl group. The peaks at 1010 and 1310 cm^{-1} can be assigned to alcools. These chelating groups would cause the efficiency of adsorption of *Carpobrotus edulis* [20, 21,22].

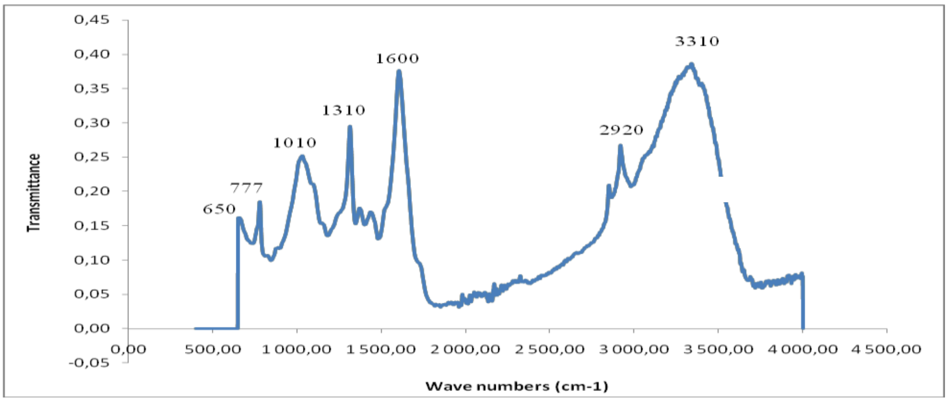

Figure3:IR spectrum of *C. Edulis.*

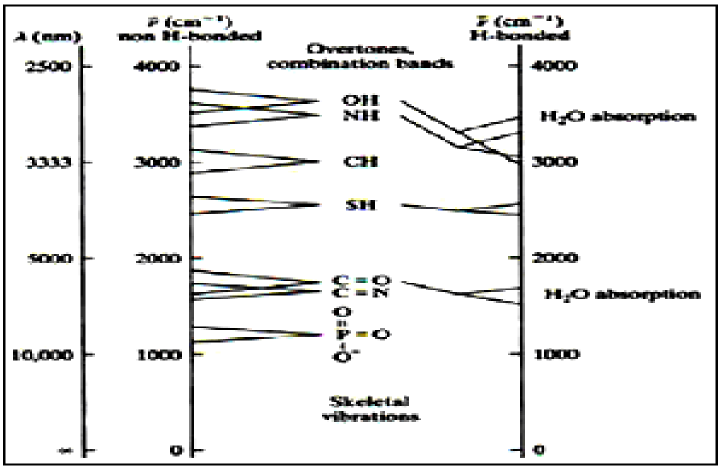

Figure4: Typicalbands of the biomolecules.

3.2. Single and Binary component systems adsorption

The studies of the binary adsorption are particularly important for the evaluation of interference degrees posed by common anions in the adsorptive treatment of the wastewaters. Figures 5 and 6 showsNO_3^- and HPO_4^{2-}adsorption on C. edulis plant in a single and binary systems.

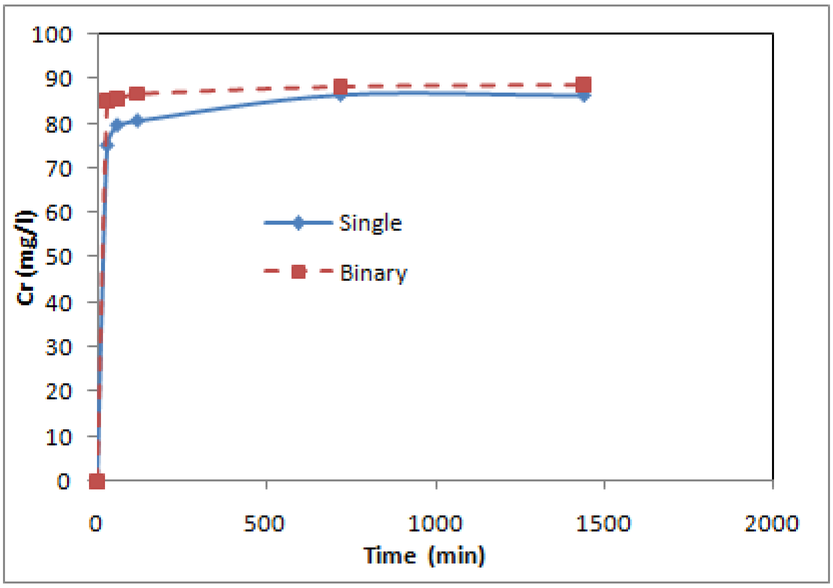

Figure5: Effect of contact time on removal of NO_3^- from single and binary component: m/v=25g/l; Ci (NO_3^-) = Ci (HPO_4^{2-}) = 100mg/l; T= 25C.

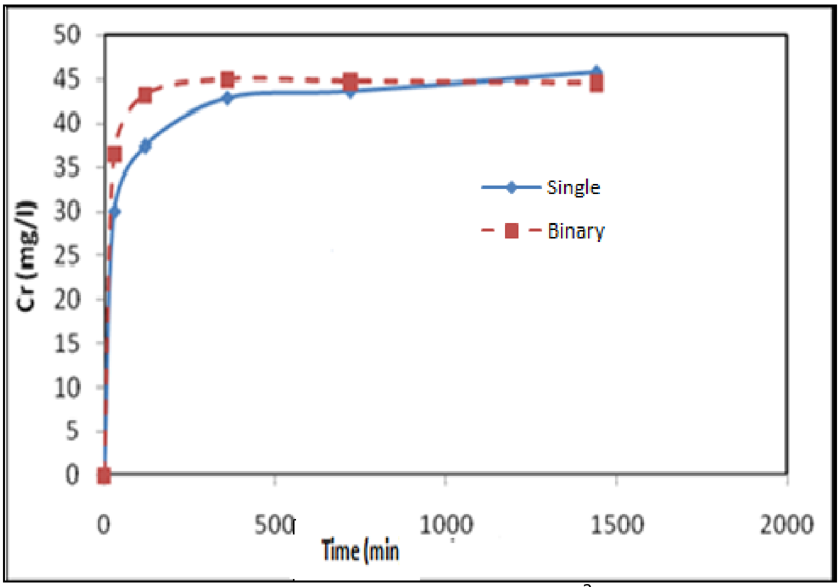

Figure5: Effect of contact time on removal of HPO_4^{2-} from single and binary component: m/v=25g/l; Ci (NO_3^-) = Ci (HPO_4^{2-}) = 100mg/l; T= 25C.

The results obtained in this study at equilibrium are presented in Table 1.

Table 1: removal of NO_3^- andHPO_4^{2-} from single and binary component (C_i = 100 mg/l, T= 25°C).

	NO_3^-	NO_3^- + HPO_4^{2-}	HPO_4^{2-}	HPO_4^{2-}+ NO_3^-
C. edulis	86,5	88,8	45,7	44,5
pH	5,8	7,3	8,5	7,3

The comparison of nitrates and orthophosphates adsorption from single and binary component shows that the concentration adsorbed increases with the time for both systems, this adsorption are identical.It was also observed that NO_3^- ions are preferentially adsorbed than HPO_4^{2-} anions. The absence of competition between these ions on the sites of adsorption can be explained by their adsorption on different sites .The structure very different from the two mineral anions is in favour of this suggestion.

This result was confirmed for the high concentration, the initial concentrations for bothanions were 3.5 g/L for HPO_4^{2-} and 4.5 g/L for ions, which are corresponding to C_{rmax} at the saturation of the solid adsorbent.The equilibrium time for nitrate ions at high initial concentrations was not affected by the addition of HPO_4^{2-} anions in the solution, while the equilibrium time for HPO_4^{2-} ions in binary solution was not affected by the addition of NO_3^- ions. The experimental adsorption capacities obtained at saturation are 2,3 g/l for $NO_3^-$and 0,4 g/l forHPO_4^{2-} In comparison to those obtained frommono-ionic systems (Table 2), the maximum experimental adsorption capacities from binary system, are identical for both anions (are the same to those obtained in single ions solution).

From these experiments, it is obvious that $NO_3^-$and HPO_4^{2-} anions can be adsorbed on different free binding sites of the adsorbent. Thus, we note that the plant micro-particles are very efficient for the removal of $NO_3^-$and HPO_4^{2-} anions in single and in binary component systems.

Table2: Removal of NO_3^- and HPO_4^{2-} from single and binary component (T=25 °C, C_{NO3}=4.5g/l, C_{HPO4}=3.5 g/l).

	NO_3^-	NO_3^-+ HPO_4^{2-}	HPO_4^{2-}	HPO_4^{2-}+ NO_3^-
C. edulis	2,5	2,3	0,5	0,4
pH	5.6	7.4	8,4	7,4

3.3. Normal and successive adsorption of nitrates and orthophosphates ions

3.3.1. Adsorption of NO_3^- by ISBM already suffers to adsorption of HPO_4^{2-}

NO_3^- solutions were prepared by dissolving a known amount of KNO_3 salts in bidistilled water. The concentration of the prepared ions solution = 50mg/l. $NO_3^-$was adsorbed by ISBM which has already used in adsorption of $HPO_4^{2-}$to equilibrium saturation (figure 6).

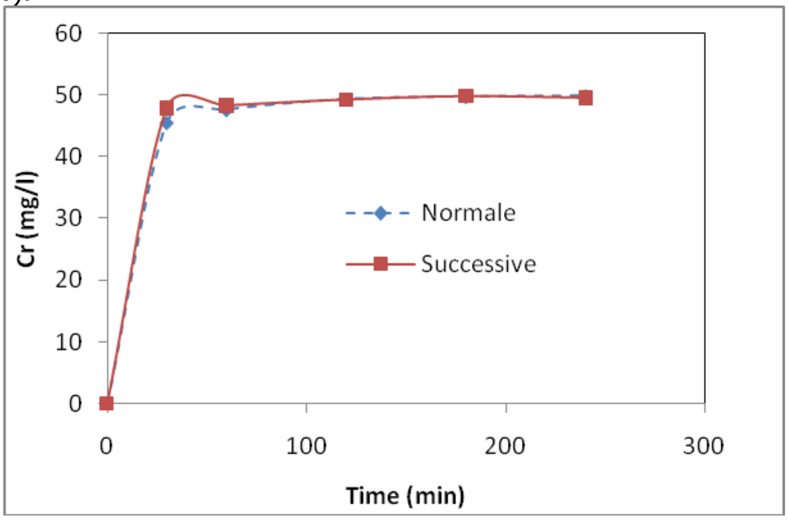

Figure6: Evolution of Cr of NO_3^- from normal and successive adsorption: m/v=25g/l; Ci (NO_3^-) = 50mg/l; T= 25C.

We note that the kinetics of the retention of nitrate ions in normal and successive Adsorption follow the same variations, these adsorptions are important (99%). These results may be due to the adsorption of these ions on different sites and would be no competition between them at the site of adsorption.

3.3.1. Adsorption of HPO_4^{2-} by ISBM already suffers to adsorption of NO_3^-

The study of the comparison between the normal and successive adsorption of HPO_4^{2-}after adsorption of NO_3^-at concentrations=50 mg/l is presented. The variation of Cr as a function of time is given in Figure 7.

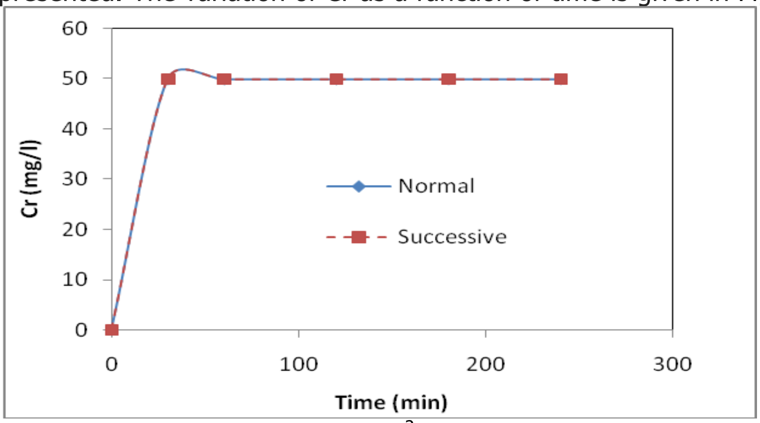

Figure7: Evolution of Cr of HPO_4^{2-} from normal and successive adsorption: m/v=25g/l; Ci (HPO_4^{2-}) = 50mg/l; T= 25C.

These results showed that the adsorptions of HPO_4^{2-} ions from normal and successive systems are identical, the retention = 100%.

4. CONCLUSION

In order to associate the performance of microfiltation to the adsorption at ISBM, the comparison of normal, successive and simultaneous adsorption of nitrate and orthophosphate in the static system by C. edulis proved of great interest. The results indicate that $NO_3^-$and HPO_4^{2-} ions are able to adsorbe on different free binding sites of the adsorbent. This study also shows that the microparticles obtained from dried C. edulis is an effective adsorbent for the removal of NO_3^- and HPO_4^{2-} from single and binary component. The goal is to use of a single membrane for several series of filtration / adsorption and their application in the treatment of polluted water or wastewater treatment.

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