

## Analysis of metal interactions in the simultaneous adsorption of Ni(II), Cu(II) and Cd(II) on olive stones activated carbon

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ARTICLE INFO	ABSTRACT/RESUME
<p><b>Article History:</b></p> <p>Received : 01/11/2016                      Accepted : 06/05/2017</p> <hr/> <p><b>Key Words:</b></p> <p>Synergism,                      Antagonism,                      Activated carbon,                      Heavy metals,                      Binary mixtures,                      Metal interactions</p>	<p><b>Abstract:</b> This article reports the synergistic and inhibitory adsorption effects involved in the multicomponent removal of heavy metal ions (Cu(II), Ni(II), Cd(II)) from binary systems using olive stones activated carbon (COSAC) as adsorbent. In order to evaluate the adsorption capacity of COSAC to remove studied heavy metals, adsorption isotherms of single and binary systems were conducted. Mono-solute adsorption isotherms fitted into Langmuir and Sips model and the maximum adsorption capacity of COSAC decreased in the order: Cd(II) &gt; Ni(II) &gt; Cu(II). In binary systems the effect of initial concentration of interfering metal ions on the removal of target ones was studied. Different mutual interactions between metals ions dealing to the decrease and the enhancement of inhibitory and synergistic effects were detected. Results showed that the effects on the adsorption of the metal ions of the binary mixture strongly depend on the initial concentration of both metal ions in the solution. In most of the sceneries studied the sum of total amount of metal ions sorbed was higher than the sum of the ones obtained in single solutions suggesting synergistic interactions between the two metal ions. This study proofs that COSAC is an effective sorbent for the removal of heavy metals from multicomponent systems.</p>

### I. Introduction

Heavy metal discharges from different industries cause surface and underground water pollution. Heavy metals, such as Cu(II), Ni(II) and Cd(II) are toxic to human beings and other living organisms even at dilute concentrations [1]. Because heavy metals are hazardous, it is necessary regulating their levels in water intended for human consumption, as well as in industrial effluents. Therefore, many organizations such as the World Health Organization [2] and Tunisian Norm [3] have given recommendations that take into account risk and

fix a maximum permissible concentration of heavy metals in wastewaters and drinking water. adsorption is the most effective process for heavy metal removal thanks to its simplicity, process with no chemical sludge and high removal efficiency even at dilute concentration (<100mg/L) [4]. The use of agriculture by-products such as: coconut fruit, nuts apricot, beet pulp, stems of tea, rice husk, pentandra hulls and olive stones-waste, which are inexpensive, abundantly available, and renewable materials, as precursor for activated carbon production reduces adsorption process cost.

Activated carbon was mainly used as effective adsorbent of heavy metals removal thanks to its highly developed pore structure, large surface area [5] and diverse acidic and basic surface functional groups, especially oxygen-containing groups (carboxylic, phenol, lactone) [6]. These authors reported that an activated carbon with high amount of carboxylic groups and low  $pH_{pzc}$  is an effective adsorbent of heavy metals. The diverse characteristics of activated carbon are incorporated by physical or chemical activation and depend on the type of precursor, activation conditions, activation agent and mode [7]. Furthermore, the non-uniform adsorption sites in AC provide complex and varied interactions during the adsorption process [8].

Adsorption of various heavy metals from single metal solutions has been extensively investigated [9-10]. However, only few publications are devoted to the studies of simultaneous adsorption of metal ions from aqueous solutions [8,11]. This is a direct consequence of the difficulty of experimentation and analysis involved in multicomponent adsorption studies. But it is a fact that natural water or wastewater effluents often contain more than one heavy metal, which can potentially modify the type of interactions (additive, synergistic and antagonistic) between metal ions that result in a competition for the adsorption sites in AC. Thus, it is important to understand the details about these interactions to better understand the exact adsorption mechanism of heavy metal adsorption onto COSAC from multicomponent systems.

Unfortunately, the majority of researchers studying multi-components adsorption processes focus on modeling adsorption data without undertaking any discussions about the interaction mechanisms that take place.

In this work, adsorption of Cu(II), Ni(II) and Cd(II) in single and binary systems onto an olive stones chemically activated carbon (COSAC) has been studied. The analysis interactions between metal ions in binary mixtures for binding adsorbent active sites were investigated by plotting isotherms of target metal containing varying initial concentration of interfering metal.

## II. Material and methods

### II.1. Chemicals

Heavy metal stock solutions of 10 mmol/L were prepared by dissolving required amounts of nickel, copper and cadmium nitrate salts in bidistilled water. Lower metal concentrations were obtained by simple dilution. An inductively coupled plasma-atomic emission spectrometer (ICP-AES; Activa-M, HORIBA JobinYvon) at 324.754 nm, 221.647 nm and 228.802 nm wavelengths was used for Cu(II), Ni(II) and Cd(II) concentration determination, respectively.

### II.2. Activated carbons preparations

The activated carbon used in this work was prepared from olive stone according to an optimized protocol [9]. The main chemical and physical characteristics of the used activated carbon (COSAC) were presented in detail in our previous works [9, 12]. Total surface area was determined using the Brunauer–Emmett–Teller (BET) equation. The elemental composition of COSAC was determined using XPS technique. The point of zero charge was determined via batch equilibrium technique [13]. Surface functional groups were determined by Boehm titration.

### II.3. Adsorption isotherms

Batch equilibrium adsorption experiments in monosolute and binary systems were conducted in isothermal conditions at  $30 \pm 1^\circ\text{C}$ . Fixed weight of AC samples of 0.3g, with average particle size of 0.375 mm, were placed into a series of 250 mL Erlenmeyer flasks containing 50 mL of metal solution. To obtain binary mixtures isotherms initial concentration of target metal ion was varied from 0.5 to 5.0 mmol/L while the initial concentration of the interfering metal ion was fixed to 0–0.5 – 1.0 – 2.0 – 3.0 – 4.0 and 5.0 mmol/L for each isotherm. In all solutions the initial pH was 5.0. The flasks were placed on a temperature-controlled multi-position magnetic shaker and shaken at 400 rpm for 10 h. This equilibrium contact time was determined in a previous work [9]. Then, after filtration through a  $0.45\mu\text{m}$  cellulose filter paper, metal solutions were diluted with nitric acid (5% by weight) to be ready for analysis.

Adsorption experiments were carried out in duplicate and the average results are presented herein.

The adsorption capacities of activated carbons were calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where  $q_e$  is the adsorption capacity (mmol/g),  $V$  is the volume of the solution (L),  $C_0$  is the initial metal ion concentration (mmol/L),  $C_e$  is the equilibrium metal ion concentration (mmol/L), and  $m$  is the mass of the activated carbon (g).

## III. Results and discussion

### III.1. Activated carbon characterization

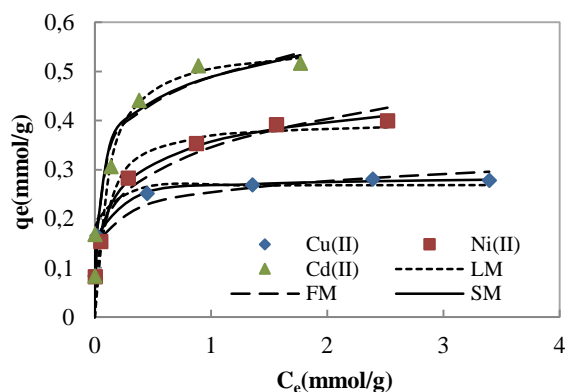
The adsorbent COSAC was characterized by a high specific surface area of  $1280\text{ m}^2/\text{g}$  and developed microporous structure. The volume of the micropores represents 98% of total of total pore volume.

Results of Boehm titration indicate that the acidic character of the adsorbent is due to the predominance of acidic functional groups such as: carbonyl, phenol and carboxylic whereas with a total acid functional group concentration of  $3.581\text{ meq/g}$  whereas the total basic functional groups concentration is  $0.198\text{ meq/g}$ . The

$pH_{pzc}$  determines the basic or acid character of the AC. The  $pH_{pzc}$  value of COSAC was found to be 3.40 and confirms the acid character of COSAC.

### III.2. Equilibrium adsorption isotherms of monosolute systems

Experimental adsorption data of Cu(II), Ni(II) and Cd(II) ions are shown in Figure 1. As can be seen, the obtained isotherms are of L-type or Langmuir type [14]. Obtained experimental isotherms were evaluated using the commonly used equilibrium models: Langmuir (Eq.(2)), Freundlich (Eq.(3)) and Sips (Eq.(5)) models.



**Figure 1:** Adsorption isotherms of Cu(II), Ni(II) and Cd(II) onto COSAC: Points represent the experimental data and lines represent modeling results by the Langmuir model (LM), Freundlich model (FM) and Sips model (SM) ( $pH\ 5$ ,  $t_{eq}\ 10\ h$ ,  $T: 30\ ^\circ C$ )

Freundlich equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where,  $K_F$  (L/g) and  $n$  are Freundlich parameters,  $K_F$  constant represents the affinity of the solute for the adsorbent whereas the constant  $n$  represents the capacitance of the adsorbent.

Langmuir equation

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

The essential characteristic of the Langmuir isotherm can be described by a separation factor which is called the equilibrium constant,  $R_L$ , defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The adsorption process is favorable for  $0 < R_L < 1$  [15].  $C_0$  is the initial concentration of the adsorbate (mmol/L).

Sips equation

$$q_e = \frac{q_{ms} \cdot K_s \cdot C_e^{ms}}{1 + K_s \cdot C_e^{ms}} \quad (5)$$

The three non-linear models parameters were determined by Solver program in Microsoft Excel.

In Figure 1 Langmuir, Freundlich and Sips nonlinear isotherms are superimposed to the experimental Cu(II), Ni(II), and Cd(II) adsorption data. The corresponding parameters of the models and correlation coefficients are illustrated in Table 1. The three models predicted quite adequately adsorption equilibrium of the studied metal ions although Sips model provided the highest correlation coefficients that ranged from 0.983 to 0.999. As seen in Table 1 the value of the theoretical maximum adsorption capacity (mmol/g) determined by the models was found to increase in the order

Cu(II) < Ni(II) < Cd(II). The  $R_L$  parameter values are lesser than 1 indicating favorable and weakly reversible adsorption of studied metal ions onto COSAC. The  $n_F$  values determined by Freundlich equation were higher than 1 indicating heterogeneous adsorption of metal ions onto COSAC.

**Table 1:** Isotherm constants for the adsorption of Cu(II), Ni(II) and Cd(II) onto COSAC from single solutions ( $pH\ 5$ ,  $t_{eq}\ 10\ h$ ,  $T: 30\ ^\circ C$ )

Isotherms	Parameters	Heavy metal ions		
		Cu(II)	Ni(II)	Cd(II)
Langmuir	$q_{e,exp} (mmol/g)$	0.278	0.400	0.516
	$q_{ml} (mg/g)$	17.080	23.460	62.911
	$q_{ml} (mmol/g)$	0.278	0.339	0.559
	$K_L (L/mmol)$	16.077	11.844	25.662
	$R_L$	0.004	0.056	0.067
	$R^2$	0.974	0.990	0.981
Freundlich	$SSR$	$3.76 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$	$5.76 \cdot 10^{-3}$
	$n$	7.920	4.364	5.958
	$K_F (mmol/L) (L/g)^{1/n}$	0.253	0.344	0.489
	$q_{mf} (mmol/g)$	0.268	0.386	0.527
	$R^2$	0.971	0.987	0.983
Sips	$SSR$	$3.64 \cdot 10^{-3}$	$3.20 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$
	$q_{ms} (mmol/g)$	0.298	0.588	2.093
	$K_s (L^m/mmol)$	8.449	1.530	0.305
	$ms$	0.467	0.437	0.198
	$R^2$	0.999	0.996	0.983
	$SSR$	$6.63 \cdot 10^{-6}$	$1.20 \cdot 10^{-4}$	$9.30 \cdot 10^{-4}$

The physicochemical properties of studied heavy metals retrieved from literature are presented in Table 2. In this work adsorption order for the studied metal ions cannot be related to the physicochemical properties of metal cations. Physicochemical properties of metal ions coupled with the steric effects of the adsorbent and physicochemical properties of its surface open the way to a multitude of interpretations that can be contradictory or even confusing. All this discussion reveals the complexity of the adsorption process of metal cations on the microporous CA.

**Table 2.** Heavy metal properties [16].

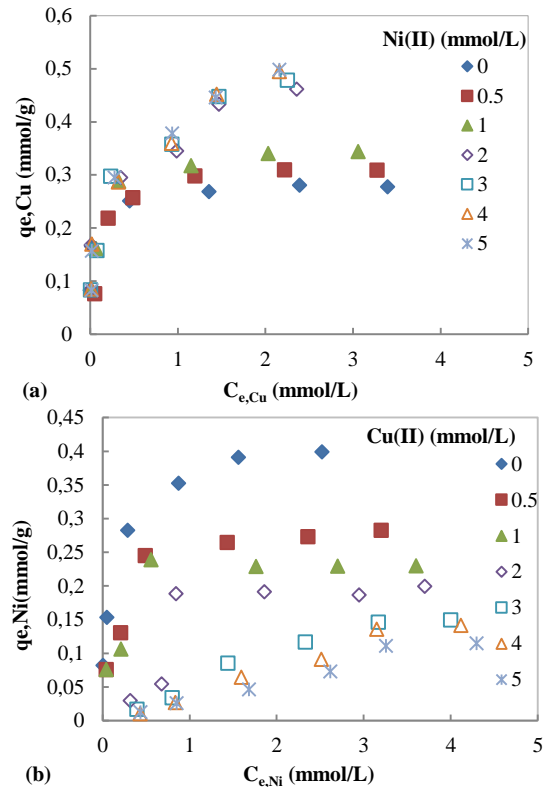
		Ni(II)	Cu(II)	Cd(II)
Molecular weight (g/mol)		58.700	63.556	112.4
Ionic radius ( $\text{\AA}^\circ$ )		0.69	0.73	0.95
Hydrated ionic radius ( $\text{\AA}^\circ$ )		4.04	4.19	4.26
Hydration energy (kJ/mol)		-2105	-2100	-1807
Electro-negativity (Pauling)		1.91	1.90	1.69
Ionization energy (eV)		18.168	20.292	16.908
Polarizability ( $10^{-24} \text{ cm}^3$ )		6.80	6.10	7.36

### III.3. Equilibrium adsorption isotherms of binary systems

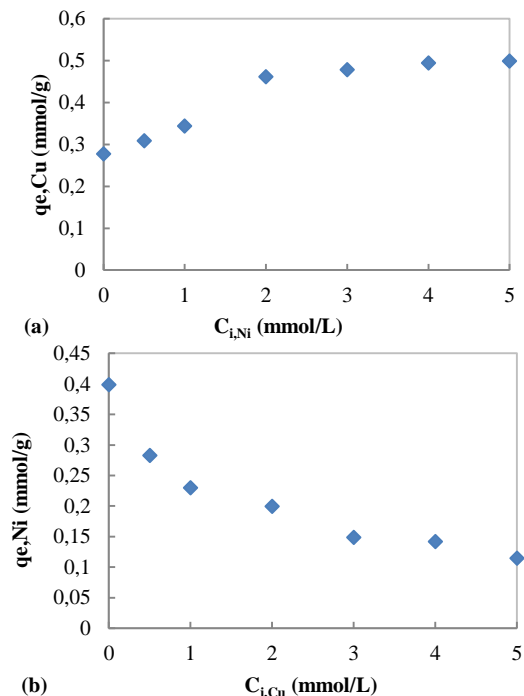
Competitive equilibrium adsorption isotherms of copper, nickel and cadmium in Cu(II)-Ni(II) and Cu(II)-Cd(II) binary mixtures are presented in Figures 2 and 4 respectively. The shapes of obtained isotherms in binary systems deviated from Langmuir type, as detected in single systems, to others forms as the concentration of the interfering metal increases. Adsorption experimental values are presented in Table 3.

#### III.3.1. Cu(II)-Ni(II) binary systems

The plot of the experimental adsorption isotherms of copper and nickel in Cu(II)-Ni(II) binary systems is depicted in Figure 2. A first glance on this Figure suggests that the presence of increasing concentrations of Ni(II) results in an increase of Cu(II) loading capacity (Figure 2 (a)) while increasing concentrations of Cu(II) exerts the contrary effect and lead to lower Ni(II) adsorption yields when in binary mixtures (Figure 2(b)). The effect of nickel on copper adsorption can be clearly shown in Figure 3 (a) where the experimental maximum amount of copper adsorbed taken from the obtained copper isotherms in binary mixtures is plotted as a function of nickel initial concentration in the mixtures. The maximum favoring effect of nickel on copper adsorption can be observed for nickel initial concentrations in the range comprised between 0 and 3.0 mmol/L where copper maximum adsorption progressively increased with the increase of nickel initial concentration. Higher nickel initial concentrations provoked only a slight increase of copper adsorption reaching a maximum value of almost double than the maximum capacity found in single solution. Villaescusa et al.[17] also reported a favoring effect of nickel on copper adsorption when studying the simultaneous adsorption of Cu(II) and Ni(II) onto grape stalks. The inhibitory effect of copper on nickel adsorption is evidenced by the plot in Figure 3 (b). Nickel maximum adsorption dramatically decreased when copper initial concentration increased from 0 to 5.0 mmol/g.



**Figure 2.** Adsorption isotherms of (a): Cu(II) in the presence of increasing initial concentration of Ni(II) and (b): of Ni(II) in the presence of increasing concentration of Cu(II) (pH: 5;  $t_{eq}$ : 10 h; T:30°C; dp:0.375mm)

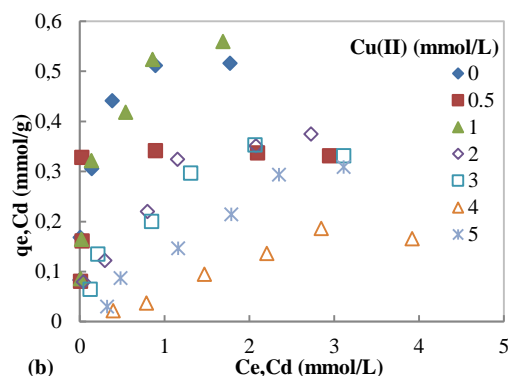
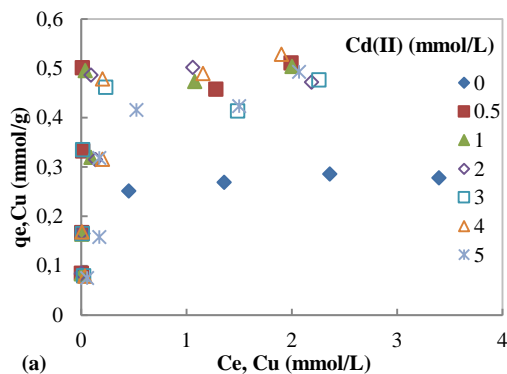


**Figure 3:** Effect of initial concentration of interfering metal in maximum adsorption of target metal (a) target metal Cu (II) interfering metal Ni(II) (b) target metal Ni(II) interfering metal Cu(II). (pH: 5;  $t_{eq}$ : 10 h; T: 30°C; dp:0.375mm).

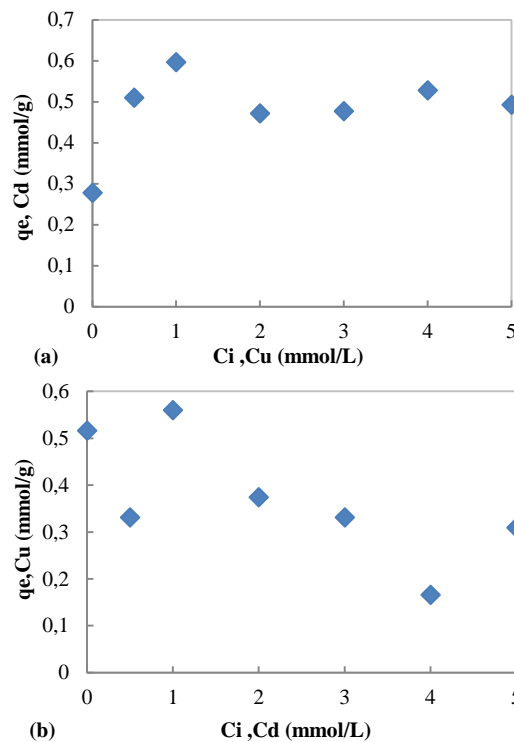
### III.3.2. Cu(II)-Cd(II) binary systems

The effect of interactions between Cu(II) and Cd(II) in binary mixtures on the adsorption of both metals onto COSAC can be seen in Figure 4. The experimental adsorption isotherms of copper in binary systems with cadmium (Figure 4(a)) show that the presence of cadmium leads to higher copper adsorption yields as compared to the one shown in single solution. Unlike the results found in the case of Cu(II)-Ni(II) binary mixtures set, copper adsorption was not higher as higher was the initial concentration of cadmium in Cu(II)-Cd(II) binary mixtures. As observed in Figure 5 (a), whose plot represents the maximum copper uptakes determined at different initial concentration of cadmium, the highest adsorbed amount of Cu(II) was obtained when cadmium initial concentration in the mixture was 1.0 mmol/L. This maximum value is more than two times the maximum amount of copper up taken in single solution. Up to this cadmium initial concentration the maximum uptake of copper slightly decreased but it was still higher than the obtained in copper single solution.

Experimental adsorption isotherms of cadmium in presence of different initial concentrations of copper are presented in Figure 4 (b). As observed in this figure, cadmium adsorption is in general inhibited by the presence of copper resulting in values of equilibrium data lower than the ones found when in single solution. Nevertheless, an initial copper concentration of 1.0 mmol/L exhibited a positive effect on Cd(II) adsorption onto COSAC surface and Cd(II) maximum uptake was slightly higher than the value obtained in single solution (8.52% of enhancement) (Figure 5 (b)). The lowest maximum adsorption data were found for the binary mixture containing 4.0 mmol/L initial cadmium concentrations. It must be remarked that variation of the amount of copper adsorbed as a function of initial concentration of cadmium did not show any clear trend.



**Figure 4.** Adsorption isotherms of (a): Cu(II) in presence of increasing initial concentration of Cd(II) and (b): Cd(II) in presence of increasing initial concentration of Cu(II) (pH: 5;  $t_{eq}$ : 10 h;  $T$ : 30°C;  $dp$ : 0.375mm).



**Figure 5:** Effect of initial concentration of interfering metal in maximum adsorption of target metal (a) target metal Cu (II) interfering metal Cd(II) (b) target metal Cd(II) interfering metal Cu(II) (pH: 5;  $t_{eq}$ : 10 h;  $T$ : 30°C;  $dp$ : 0.375mm).

### III.3.3. General discussion

Table 3 summarizes the experimental adsorption values obtained for the studied metals both in single ( $q_{max,i \text{ single}}$ ) and binary mixture ( $q_{max,i \text{ binary}}$ ) the total amount of metal ions sorbed ( $q_{max,tot}$ ) and the ratio between metal maximum adsorption in single solution and in binary mixture ( $q_{max,i \text{ binary}} / q_{max,i \text{ single}}$ ). As seen in table 3 adsorption of copper is always favored by the presence

of both nickel and cadmium which indicating an enhancement effect. The amount of copper sorbed increased from 0.278 mmol/g its maximum adsorption in single solution to around 0.500 mmol/g with the increase from 0 to 5mmol/L the initial concentration of nickel and cadmium, respectively. Similar amount of maximum copper sorbed was also attained in the cadmium and nickel isotherms when copper initial concentration was 5.0 mmol/L. On its turn, 5.0 mmol/L initial concentration of copper reached a maximum adsorption around 0.500 mmol/g with independence whether it is in single or in binary mixture.

Adsorption results of the studied metals in binary mixtures reveal a new metals affinity order  $\text{Cu(II)} > \text{Cd(II)} > \text{Ni(II)}$ . Gwenzi et al [18] also found that the affinity order  $\text{Cd(II)} > \text{Cu(II)}$  found in monosolute solutions changed to  $\text{Cu(II)} > \text{Cd(II)}$  when the metals were forming binary mixtures. As seen in Table 3 the sum of the maximum adsorption values of both metals in binary mixtures ( $q_{\text{max, tot}}$ ) is in most of the cases less than the sum of those in single solutions indicating that the joined effect on each other metal is antagonistic. Antagonistic effects were also reported in literature [19-20]. Conversely a synergistic effect was observed in the case of  $\text{Cu(II)}-\text{Cd(II)}$  isotherms when cadmium initial concentration were 4.0 and 5.0 mmol/L. Synergistic effects were also reported by Luo et al. [8] for heavy metals adsorption onto activated carbon. The last column in Table 3 corresponds to the ratio between the maximum amount of target metal adsorbed in single solution and in binary mixtures. Ratios higher than unity indicate that the presence of a second metal enhances adsorption of the target metal (i), ratios equal to unity no effect on adsorption of the interfering metal and lower than unity inhibitory effect on target metal adsorption [21].

Ratios corresponding to copper are always higher than unity, increase with the increase of interfering metal and range between 1.111 and 1.795 and 1.697 and 1.899 when the interfering metal is nickel and cadmium, respectively. Values around unity mean that both metals exert little enhancing or suppressing effects on each other adsorption. In the case of  $\text{Cd(II)}-\text{Cu(II)}$  binary mixture cadmium adsorption ratios only slightly exceeded unity when initial concentration was 0.5 mmol/L and the rest of

values were far from unity confirming the inhibitory effect of copper on cadmium adsorption.

#### IV. Conclusion

An activated carbon (COSAC) prepared from low cost olive stones agriculture by-product, characterized by a low  $\text{pH}_{\text{pzc}}$  and predominance of acidic functional groups on its surface, was used as sorbent for  $\text{Cd(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cu(II)}$ . From the obtained results the following conclusions can be retrieved:

- COSAC shows a significant capacity to remove studied metal ions from single solution and binary mixtures.
- Adsorption data of the studied metals in single solution were well predicted by Langmuir and Sips models and maximum capacity of COSAC for each of the metals decreased in the order  $\text{Cd(II)} > \text{Ni(II)} > \text{Cu(II)}$ .
- In binary systems maximum capacity of COSAC for each of the metals resulted influenced by the presence of a second metal. A new order of maximum capacity of COSAC for each of the metals was observed  $\text{Cu(II)} > \text{Cd(II)} > \text{Ni(II)}$ .
- $\text{Cu(II)}$  presented a strong inhibitory effect on  $\text{Cd(II)}$  and  $\text{Ni(II)}$  adsorption in  $\text{Cu(II)}-\text{Cd(II)}$  and  $\text{Cu(II)}-\text{Ni(II)}$  binary mixtures; however,  $\text{Cd(II)}$  and  $\text{Ni(II)}$  enhanced  $\text{Cu(II)}$  uptake in the same binary systems.
- The amount of copper sorbed of binary mixtures was always higher than that of copper single solution.
- In most of the binary systems the net interactive effect between the metals forming the mixtures was found to be antagonistic as the total amount of metal sorbed was lesser than the sum of individual maximum capacity found in single metal solutions. However, a synergistic effect was observed in the case of  $\text{Cu(II)}-\text{Cd(II)}$  at high initial concentrations.

Finally, this work highlights the important influence of the initial concentration of the interfering metal on mutual metal interactions that result in both inhibitory and enhancing effects on metals adsorption. This work opens the way for further research to better understand the exact adsorption mechanism of heavy metal adsorption onto COSAC from multicomponent systems.



Table 3: Metal adsorption experimental values in single and binary mixtures (pH 5,  $t_{eq}$ : 10 h,  $T$ : 30 °C)

	$C_0$ (mmol/L) of interfering metal ion	single $q_{max,i}$ (mmol/g)	binary $q_{max,i}$ (mmol/g)	binary $q_{max,j}$ (mmol/g)	$q_{max,tot} = q_{max,i}^{binary} + q_{max,j}^{binary}$ (mmol/g)	$q_{max,i}^{binary} / q_{max,i}^{single}$
<b>Cu(Cu-Ni)</b>	0.5	0.278	0.309	0.013	0.322	1.111
	1		0.344	0.015	0.359	1.237
	2		0.462	0.046	0.508	1.661
	3		0.478	0.074	0.552	1.719
	4		0.499	0.107	0.606	1.795
	5		0.499	0.089	0.588	1.795
<b>Ni(Ni-Cu)</b>	0.5	0.399	0.283	0.083	0.366	0.707
	1		0.230	0.157	0.387	0.575
	2		0.200	0.295	0.495	0.500
	3		0.150	0.378	0.528	0.375
	4		0.142	0.446	0.588	0.355
	5		0.115	0.499	0.614	0.287
<b>Cu(Cu-Cd)</b>	0.5	0.278	0.510	0.030	0.540	1.834
	1		0.503	0.065	0.568	1.809
	2		0.472	0.191	0.663	1.697
	3		0.476	0.098	0.574	1.712
	4		0.528	0.551	1.079	1.899
	5		0.493	0.493	0.986	1.773
<b>Cd(Cd-Cu)</b>	0.5	0.516	0.331	0.075	0.406	0.641
	1		0.560	0.158	0.718	1.085
	2		0.374	0.472	0.846	0.724
	3		0.331	0.415	0.746	0.641
	4		0.166	0.423	0.589	0.321
	5		0.309	0.493	0.802	0.598

i: target metal ion; j: interfering metal ion

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