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Single and binary adsorption of some heavy metal ions from aqueous solutions by activated carbon derived from olive stones

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ABSTRACT

In the present work, activated carbon synthesized from olive stones was used for heavy metal ions (Cu(II), Ni(II), and Pb(II)) removal in single and binary aqueous solutions. The effect of initial solution pH was studied. The equilibrium isotherms for single systems were evaluated in terms of maximum adsorption capacity and adsorption affinity by the application of Langmuir model. Metal ions adsorption increases in the following order: Pb(II) > Ni (II) ≥ Cu(II). The examination of binary adsorption systems: Cu–Ni and Cu–Pb shows that the affinity of copper on the activated carbon surface was strongly dependent on initial concentration of nickel and lead. Copper adsorption was found to increase in the presence of nickel and to decrease in the presence of lead.

Keywords: Activated carbon; Olive stones; Copper; Nickel; Lead; Heavy metal; Adsorption; Single; Binary

1. Introduction

Harmful, carcinogenic, and non-biodegradable toxic heavy metals are widely detected in contaminated water discharged from various industries such as mining, storage batteries, metallurgical, tannery, and chemical manufacturing. Nickel, copper and lead are heavy metal of environmental concern; they belong to the list of the main toxic heavy metals (Cu, Ni, Zn, Cd, Pb, Cr), which are subject of many researches [1–3]. Their concentrations in industrial effluents are very high and can reach 16,000 mg/L for nickel, 100–120 mg/L for copper [4], and 200–500 mg/L for lead [5].

Efforts to reduce hazardous heavy metals from water effluents have become one of the most important environmental challenges that the world faces today. The World Health Organization [6] recommended as the maximum allowed concentration values in drinking water for copper, nickel, and lead to be less than 2.0, 0.2, and 1.0 mg/L, respectively. For example, the Pollution Control Department [7] has

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recommended the maximum acceptable concentration of copper, nickel, and lead metal ions in wastewater effluents as 1.0, 2.0, and 0.2 mg/L, respectively.

Conventional processes have been applied to remove heavy metals from wastewaters. Among these processes, adsorption on activated carbon is considered as one of the most practical and economical water treatment process.

On other side, using agriculture by-products as precursor for activated carbon production, for water treatment, reduces the adsorption process cost. Olive stones are an agricultural waste predominantly produced in the Mediterranean countries such in Tunisia, ranked as the fourth largest world producer of olive oil. The main objectives of this work are to valorize waste olive stones supplied from Tunisian oleic factories and evaluate it as an adsorbent for copper, nickel, and lead metal ions from aqueous phase. Several works have been focused on the application of various adsorbents for the removal of single solute heavy metal ion from the aqueous phase [8,9]. However, only a few publications are devoted to the binary or the multi-solute adsorption [9,10] that is more important to study and evaluated since single toxic metal species rarely exists in natural water and wastewater. Experimental work interested by heavy metal adsorption equilibrium could confirm the benefits of activated carbons prepared from olive stones adsorbent in single and binary solute systems.

2. Materials and methods

2.1. Adsorbent, chemicals, and equipments

This olive stones waste, composed largely of cellulose, hemicelluloses and lignin, is used as precursor for activated carbon preparation. Olive stones were firstly impregnated with phosphoric acid solution at 50 wt.% at 110˚C for 9 h. Then the dried solid was subjected to thermal activation in a nitrogen atmosphere in a horizontal tubular reactor at 410˚C for a reactive time of 150 min. The final washed and dried activated carbon was crushed and sieved to the desired particle size (average diameter of 0.375 mm) to be used as adsorbent materials in experiments.

The adsorption characteristics of activated carbon are generally related to physical proprieties and chemical properties of the carbon surface [11]. The specific surface area, pore volumes, and pore size distribution were determined for activated carbon produced from olive stones (COSAC) using nitrogen sorptiometry at 77 K on the automatic Quantachrome AS1-C apparatus in the range of relative pressure from 10^{-5} to 1.0.

Scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) was used to observe the morphology of the synthesized COSAC.

The Boehm method is used for determination of acidic and basic surface groups. Furthermore, the pH at the point of zero charge (pH_{PZC}) of the activated carbon, namely the pH value required to give zero net surface charge, was measured using mass titration method [12].

Analytical grade of nitrate salts of heavy metals was used for the preparation of different metal ions solutions. All working solutions were prepared by diluting the stock solutions of 1 g/L with ultrapure water. Solutions of 0.1 M NaOH and 0.1 M HNO_3 were used for pH adjustment. Initial and residual metal ions concentrations were determined by flame atomic absorption spectrometry (VARIAN Absorption Spectrometer-Model220FS-).

2.2. Adsorption experiments

The metal ions chosen for the investigation in single-component system were Cu(II), Ni(II), and Pb (II), and in binary systems investigations, two systems: Cu(Cu–Ni) and Cu(Cu–Pb) were considered. Equilibrium experiments were conducted on batch mode at 30 ± 2˚C. To obtain the adsorption equilibrium isotherms, 0.3 g of COSAC samples was placed into 250-ml glass-stoppered conical flasks containing 50 mL of metal ions solutions having different initial concentrations within the range of 0.5–5.0 mM for Pb(II), Cu(II), and Ni(II) metal ions. The flasks were agitated for 10 h at 400 rpm. Then, samples were filtrated through a 0.45-μm cellulosic filter paper. During the experiments, the temperature was maintained at 30 ± 2˚C by using a thermostatic bath.

Evaluation of initial solution pH effect on the adsorption of Cu(II), Ni(II), and Pb(II) on COSAC was undergone in the same conditions as indicated above with an initial metal ions concentration of 1 mM and an equilibrium time of 10 h. Initial pH solutions were adjusted within the range of 2.0–6.0 by adding given volume of 0.1 M NaOH or 0.1 M HNO_3.

Binary adsorption isotherms have been obtained by fixing initial concentration of interferential metal ions and varying the concentration of the target metal ions over the range 0.5–5.0 mmol/L.

The amount of metal ion uptake by COSAC was calculated using the following equation:

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

where C_0 is the initial metal concentration in the solution (mM), C_e is the metal concentration remaining in the solution at equilibrium time (mM), m is the weight of COSAC (g), q_e is the metal ion uptake (mmol g^{-1}), and V is the volume of solution in the flask (L). Each experiment was carried out in duplicate and the average results are presented here.

3. Results

3.1. Characterization of activated carbon

3.1.1. Physical characteristics

The nitrogen gas adsorption–desorption isotherm of the synthesized COSAC at 77 K is given in Fig. 1. The isotherm appears to have a well-defined plateau and classified as Type I according to UIPAC classification. Strong adsorption occurring at low relative pressures (less than 0.2) indicates a highly microporous material with narrow pore size distribution. The N_2-isotherm shows also a small effect in desorption curve, showing the presence of mesopores with possible occurrence of capillary condensation phenomenon. The micropores and mesopores volumes were calculated to be 0.558 and 0.013 cm^3/g, respectively (Table 1), so micropores take about 98% of the total pore volume and this asserts that COSAC is a microporous structure material. The pore size distribution evaluated by Barret–Joyner–Halenda (BJH) method and illustrated in Fig. 2 confirms the microporous structure of olive stones activated carbon.

This conclusion implies that our synthesized activated carbon is highly appropriate for the removal of ions molecules with small particle sizes (less than 30 Å). Textural characteristics analysis summarized in Table 1 indicates that the adsorbent has a large specific surface area (1,081 m^2/g).

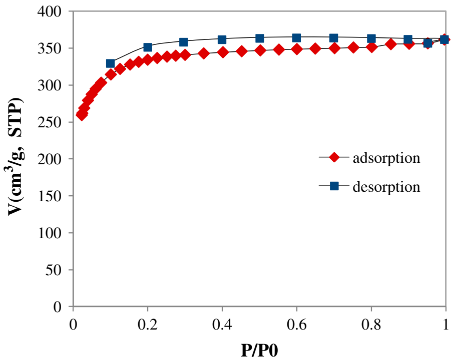

Fig. 1. Nitrogen adsorption–desorption isotherm at 77 K of COSAC.

Table 1
Properties of COSAC

Physical properties	
Total area (BET)	1,081 m^2 g^{-1}
Micropore volume	0.558 cm^3 g^{-1}
Total pore volume	0.571 cm^3 g^{-1}
Average pore diameter	19.16 A˚
pH_{pzc}	3
Surface functional groups (meq g^{-1}):	
Carboxylic groups	0.100
Carbonyl groups	2.720
Lactonic groups	0.300
Phenolic groups	1.650
Total basic groups	0.750
Element analyses by EDX (wt.%):	
Carbon	87.60
Oxygen	10.46
Phosphorus	1.93

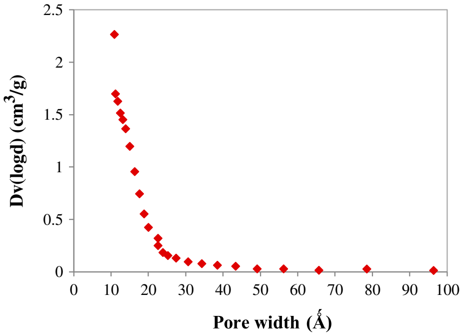

Fig. 2. Pore size distribution of COSAC.

The surface structure of COSAC was analyzed by SEM (Jeol JSM-6400) coupled with EDX (Table 1). The SEM image shows that the microscopic shape of COSAC is an agglomeration of sub micrometric particles (Fig. 3).

Elementary analyses determined by EDX show the presence of a small percentage of phosphor presumably inserted in the complex carbon structure.

Physical COSAC properties show a high specific surface area and developed micropores.

3.1.2. Chemical characteristics

Some functional groups occurred on the surface of COSAC are determined by Boehm titration. Results of surface functional groups reported in Table 1 indicate the predominance of acidic functional groups on the COSAC surface, especially carbonyl and phenolic functional groups, resulting in 4.77 meq g^{-1} of total acidity. The use of phosphoric acid in the activation process provides a high amount of acid groups on the

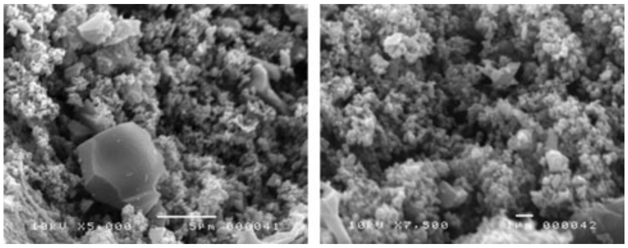

Fig. 3. Scanning electron micrographs of COSAC.

activated carbon surface. Whereas total basicity accrues on COSAC surface was only 0.75 meq g^{-1}. It known that the amount of basic and acidic functional groups of a given activated carbon strongly depends on the activated carbon preparation conditions and on the nature of the precursor. The relative amounts of acidic-basic surface groups determines the pHpzc, that is the point of zero charge describes the pH solution value when global electrical charge density on surface adsorbent is zero. Table 1 gives the value of $pH_{pzc} = 3$ of COSAC showing acidic character of COSAC. At pH < pHpzc, the carbon surface has a net positive charge, while at pH > pHpzc the surface has a net negative charge which favors the binding of heavy metal cations by electrostatic attraction.

3.2. Effect of initial solution pH

Fig. 4 shows that metal adsorption is strongly pH-dependent and increases with the pH until it reaches a maximum at around pH 5. The removal percentage of copper, nickel, and lead increased from 16.4% to 62.0%, from 21.0% to 78%, from 34.0% to 97.0%, and from 50.0% to 100%, respectively, when initial pH increased from 2.2 to 5.5. The low adsorption at low pH is due to the competition between protons and metal ions for the same adsorption sites. The effect of pH can also be explained by considering the sorbent surface charge. COSAC $pH_{pzc} = 3$ indicates that for initial pH lower than 3, the surface of the COSAC is positively charged and metal adsorption is inhibited, due to electrostatic repulsion between metal ions and positively charged functional groups. Inversely, for pH > 3, the number of negatively charged sites on COSAC surface increases, and metal adsorption becomes more important.

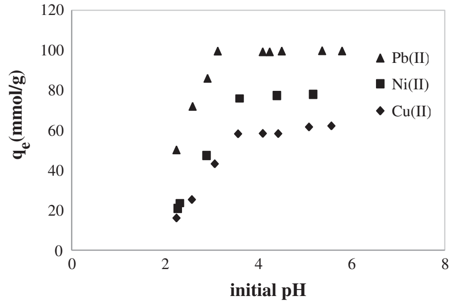

Fig. 4. Effect of initial solution pH on the removal of Pb (II), Ni(II) and Cu(II). (C_0: 1 mmol/L, equilibrium time: 10 h, temperature: 30˚C).

In most of the reported studies concerning metal ions adsorption onto activated carbon adsorption uptake shows a maximum for initial pH around 5 [13,14]. Based on these results, the best initial pH for these metallic ions adsorption was considered to be 5, and all equilibrium experiments were carried out at this pH.

3.3. Adsorption equilibrium isotherms of Cu(II), Ni(II), and Pb(II)

3.3.1. Single solute

The adsorption isotherms of Cu(II), Ni(II), and Pb (II) onto COSAC were studied at 30˚C and an initial solution pH of 5. Adsorption isotherms data of the three heavy metal ions are reported in Fig. 5. The shapes of the isotherms are similar and show L-type behavior according to Giles and Smith classification [15] but differ in the amount of metal adsorbed. The shape of isotherms shows substantial affinity between the COSAC surface and the three heavy metal ions, especially for lead and weaker competition with the solvent molecular. The removal of each metal ion increased with the initial metal concentration while the metal-removal efficiency decreased which was known as the loading effect, describing the extent to which the total number of sorption sites is occupied by the sorbate [16].

The experimental adsorption data are fitted with Langmuir and Freundlich models.

The Langmuir equation can be presented as follows:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where C_e (mmol/L) is the equilibrium concentration metal ion in solution; q_e (mmol/g) is the surface concentration of metal ion at equilibrium; $q_{\max}$ (mmol/g) is the amount of metal ion adsorbed at complete monolayer coverage; K_L (L/mmol) is a constant that relates to the heat of adsorption.

The Freundlich model can take the following form:

$$q_e = K_F C^n \tag{3}$$

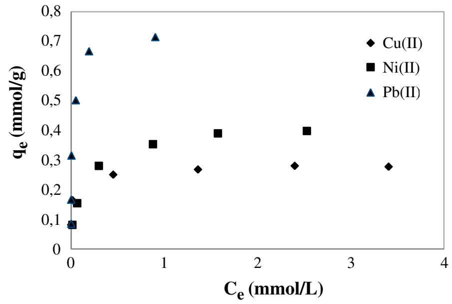

Fig. 5. Adsorption isotherms of Cu(II), Ni(II) and Pb(II) onto COSAC (pH: 5, equilibrium time: 10 h, temperature: 30°C).

where K_F (mmol/g (mmol/L)$^{-n}$) represents the adsorption capacity when metal ion equilibrium concentration (C_e) equals 1; n represents the degree of dependence of adsorption on equilibrium concentration.

The Langmuir and Freundlich model parameters estimated directly by using the nonlinear regression and correlation coefficients (R^2) are illustrated in Table 2.

Langmuir model predicts the experimental data perfectly with higher correlation coefficients ($R^2 > 0.997$). The value of the maximum adsorption capacity determined by Langmuir model was found to increase in the order Cu(II) < Ni(II) < Pb(II). This order of metal removal is consistent with the ionic radii of hydrated ions. Pb(II) has the largest ionic radius (1.19A°) followed by those of Ni(II) (0.69A°) and Cu(II) (0.67A°). The bigger the ionic radius, the stronger the adsorption of the ion since the hydration capacity of that ion is smaller, resulting in weaker binding of the ion and water phase [14]. The examination of K_L values demonstrates that adsorption of Pb (II)(K_L = 126.02) was more favorable than that of nickel (K_L = 40.508) and copper (K_L = 11.439).

Freundlich parameters and R^2 values reported in Table 2 indicate that this model showed lower correlation with the experimental adsorption data as compared to the Langmuir model. The highest adsorption capacity of Pb(II) can be illustrated by K_F values 0.944, 0.348 and 0.257 for Pb(II), Nickel(II), and Cu(II), respectively. The small n values (less than unit) suggest the favorable adsorption of the studied metal ions onto COSAC.

In comparison with other activated carbons studied in other published works for the same metal ions adsorption, the adsorption order changes strongly from one adsorbent to another (Table 3). When looking at the results in the table, it seems that the difference in adsorption affinity order and adsorption amount may be related not only to metal ions properties but also to physical–chemical properties of the adsorbent (morphology, surface area, pores disruption, functional groups). The reason for this is that a substance which is a good adsorbent for one adsorbate may not be a good adsorbent for other species.

Table 3 lists a comparison of maximum adsorption capacities of different adsorbents toward the metals under study, note that these data have been obtained at different conditions. It can be seen that COSAC has a relatively high adsorption capacities 17.78, 24.067, and 148.77 mg g^{-1} for Cu(II), Ni(II), and Pb(II) ions,

Table 2
Langmuir and Freundlich parameters

Metal ion	Langmuir parameters			Freundlich parameters		
	q_{max} (mmol/g)	K_L (L/mmol)	R	K_F (mmol/g) (mmol/L^3)$^{-n}$	n	R^2
Cu(II)	0.280	11.439	0.999	0.257	6.756	0.934
Ni(II)	0.410	40.508	0.997	0.348	3.921	0.986
Pb(II)	0.718	126.02	0.999	0.944	3.921	0.798

Table 3
Comparison of maximum adsorption capacities (mg g^{-1}) with various adsorbents for different metal ions

Adsorbent	Conditions	Cu(II)	Ni(II)	Pb(II)	References
Granular A.C	pH 5	15.58		15.58	[16]
Powdered A.C		26.9		26.90	
Apricot stone A.C	pH 6.5; 25°C	24.08	26.9	22.84	[8]
Carbon nanotube	pH 5	28.595		96.969	[10]
Bamboo activated carbon	pH 5; 23°C	7.371	6.457	–	[11]
COSAC	pH 5; 30°C	17.780	24.067	148.77	This study

respectively. Therefore, COSAC has a significant potential for the removal of these metal ions from aqueous solution.

3.3.2. *Adsorption of Cu(II), Ni(II), and Pb(II) in binary systems onto COSAC*

A toxic metal ion rarely exists alone in natural water or wastewater effluents. For that it is necessary to take into consideration the presence of other species. The competitive adsorption equilibrium isotherms for Cu(II)–Ni(II) and Cu(II)–Pb(II) binary solutes systems were obtained by fixing initial concentration of interferential metal ions and varying the concentration of the target metal ions over the range 0.5–5 mmol/l.

3.3.2.1. Cu(II)–Ni(II) binary system. Binary system obtained is reported in Fig. 6. One observes that the adsorbed amount of copper increased with the increasing initial concentration under the fixed concentration of nickel as the background, and the trend was similar to that of the single solute. This figure also shows that the capacity of COSAC to remove copper increases with increasing in the initial concentration of nickel, obviously in the highest concentration. Up to an initial concentration of nickel equal to 2.00 mmol/L, the adsorbed amount of copper shows a little enhancement. The maximum uptake toward copper was enhanced from 0.27 mmol/g in single system solution to 0.48 mmol/g with the coexistence of 5 mmol/L nickel.

3.3.2.2. Cu(II)–Pb(II) binary system. During the adsorption of Cu(II) onto COSAC, the presence of Pb (II) displayed a positive effect on the adsorption of Cu (II) onto COSAC for an initial concentration of 0.5, 1, and 2 mmol/l, and a negative effect, with initial concentration of 3, 4, and 5 mmol/L, especially at low concentrations of copper, however, for copper initial concentration up than 3 mmol/L the presence of lead has no effect on copper removal (Fig. 7).

The antagonist observed behavior can be explained by the competitive effects on the active adsorption sites, especially at low concentrations.

There are several possible explanations for these results, although all of them should be attributed to strictly physical effect in the adsorption process and the affinity of each metal ion for specific carbon functional groups. For Cu(II)/Ni(II) system, the amount of copper removal in the presence of nickel as compared to single metal solution. The observation must be due to the competitive effect inducing enhancement effect the affinity and reaction between copper and carbon acidic functional groups.

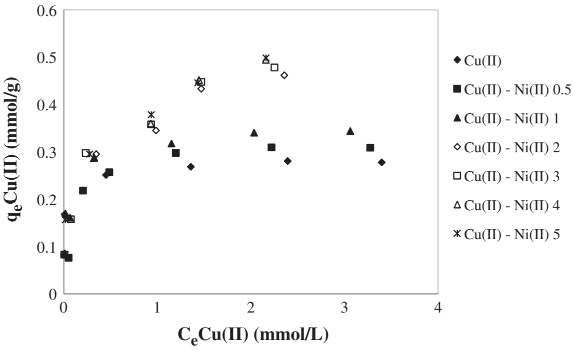

Fig. 6. Adsorption isotherms of Cu(II) in binary system (Cu–Ni) (pH: 5, equilibrium time: 10 h, temperature: 30°C).

Gao et al. [17] found the same trend when they studied the adsorption of copper and nickel metal ions onto oxidized carbon nanotubes. These authors explained their results by the fact that since Ni(II) is considered to be more weakly adsorbed species; it is displaced by copper as the concentration of the solution increases and they propose that the electronegativity plays an important role in competitive adsorption.

The same behaviors registered Cu(II)/Pb(II), the affinity of copper increases firstly for lower concentration of lead then decreases for lead concentration up than 3 mmol/L because the lead ion radii are larger than of nickel that is why there is a limit of competition effect between copper and copper for high concentration.

The analogue trend was observed by Sheng et al. [18]. However, Wang et al. [19] found that Pb(II) ion is always favorable adsorbed on bone char over Cu(II) in binary mixture systems. These authors related the strong competitive effect of lead to the selectively of ion exchange and to the difference in the hydrated ionic radii. This result is similar to that obtained by Lee and Moon [20] and Lv et al. [21] despite the difference in the adsorbent material.

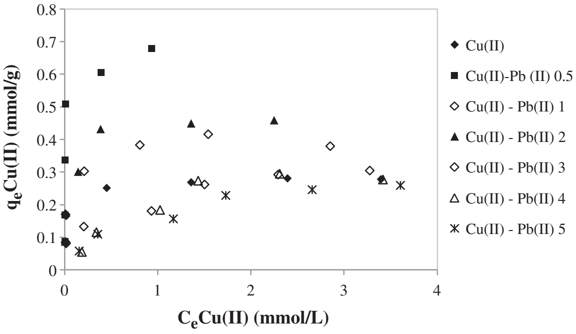

Fig. 7. Adsorpton isotherms for Cu(II) in binary system (Cu–Pb) (pH: 5, equilibrium time: 10 h, temperature: 30°C).

4. Conclusion

The removal of heavy ionic metals from aqueous single and complex solutions by adsorption on olive stone activated carbon produced by thermo chemical process using phosphoric acid (COSAC) was investigated. The examination of initial pH effect on copper, nickel, and lead removal shows that metal adsorption is pH-dependent and maximum adsorption was found to occur with initial pH 5. The impregnation with phosphoric acid gives to COSAC acidic functional groups characteristic—transpose by the lower pHpzc, high surface area, and developed micropores. These characteristics enhance the affinity of metal ions to be adsorbed on COSAC surface, and this was demonstrated by the amount adsorbed of each metal ion as compared to other adsorbent. The experimental equilibrium adsorption data are better fitted by the Langmuir model and the adsorption capacity of COSAC decreased in the order: Pb(II)>Ni(II)>Cu(II). Binary adsorption study shows a good affinity for copper to carbon surface more than nickel and Lead. The examination of binary adsorption systems: Cu–Ni and Cu–Pb shows that the affinity of copper on prepared activated carbon surface was strongly dependent on initial concentration of nickel and lead. The adsorption amount of copper increased in the presence of nickel and decrease in the presence of lead.

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