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Comparative Study of Bivalent Cationic Metals Adsorption Pb(II), Cd(II), Ni(II) and Cu(II) on Olive Stones Chemically Activated Carbon

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Abstract

In this work the ability of olive stone activated carbon (COSAC) to remove Pb(II), Cd(II), Ni(II) and Cu(II) metal ions from aqueous solutions was evaluated. The effect of initial pH, contact time and initial concentration on metal ions adsorption was investigated. The results indicated that pH 5 is the optimum value for metal removal. Adsorption kinetic rates were found to be fast; total equilibrium was achieved after 4 hours. Kinetic experimental data fitted very well the pseudo-second order equation and the values of adsorption rate constants were calculated. The equilibrium isotherms were evaluated in terms of maximum adsorption capacity and adsorption affinity by the application of Langmuir and Freundlich equations. Results indicate that the Langmuir model fits adsorption isotherm data better than the Freundlich model. The removal efficiency of heavy metal ions by COSAC decreases in the order Pb(II) > Cd(II) > Ni(II) ≥ Cu(II).

Keywords: Heavy metal ions; Adsorption; Activated carbon olive stones; Kinetic; Equilibrium

Introduction

Environmental pollution by heavy metals has become one of the most hazard problems due to their dangerous effect on aquatic flora and fauna even in relatively low concentrations. Several heavy metal ions such as copper, nickel, cadmium and lead have been included in the U.S. Environmental Protection Agency's list of priority pollutants [1]. Copper leads to toxic effects including liver damage and gastrointestinal disturbances. Nickel is a well-known human carcinogen, particularly in human lung cancer [2]. Cadmium causes renal dysfunctions, hypertension and diabetes [3], and Lead is highly hepatotoxic [4]. Many industrial processes, such as smelting, metal plating, mining pigments, cadmium-nickel-batteries, brass manufacture and discharge aqueous effluents containing high levels of these heavy metal ions. Various physical and chemical processes have been extensively used to remove heavy metal pollutants from aqueous solutions such as chemical precipitation, ion exchange, bioadsorption, adsorption, membrane filtration, etc. Adsorption on activated carbon is considered one of the most widely applied techniques for pollutants removal from contaminated media owing to its efficiency especially at low concentrations and process simplicity. Most research has been focused to the adsorption of heavy metals by activated carbon prepared from different precursors, these include apricot stone [5], bamboo [6], the olive pulp, cherry stones, rice husks etc. Many factors can influence the degree of adsorption of metal ions on activated carbon especially. In one side one must take account of: (i) solution pH, solutes nature and concentration, physicochemical properties of metal ions e.g. speciation, ionic radius, hydration energy and electro-negativity. In other side one must consider the sorbent characteristics as (i) the point of zero charge of the sorbent surface (pH_{pzc}); (ii) sorbent specific surface area and porosity; (iii) sorbent surface functional groups. Some of these adsorbent properties are related to the activation process and oxidation agent.

The aim of this work was to evaluate the adsorption capacity of olive stone carbon chemically activated as well as to investigate adsorption equilibrium and kinetics of copper, nickel, cadmium and lead divalent ions from aqueous solutions.

Experimental

Chemicals and equipments

All chemicals used in the present study were of analytical grade. Stock metal solutions of 1 gL^{-1}were prepared by dissolving in Milli-Q water quality appropriate amounts of $Cu(NO_3)_2.6H_2O$, $Ni(NO_3)_2.12H_2O$, $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$. The stock solution of each nitrate salt was diluted to get the desired initial metal ion concentration (C_0). Different diluted metal concentrations prepared from Cu(II), Ni(II), Cd(II) and Pb(II) standard solutions (1 gL^{-1} for FAAS, Merck) were used to obtain the calibration curves for Flame Atomic Absorption Spectrometry (VARIAN Absorption Spectrometer (Model220FS)). Solutions of NaOH (0.1 M) and HNO_3 (0.1 M) were used for adjusting the pH.

Adsorbent

Olive stones activated carbon (COSAC) produced by chemical activation, according to Ghrib et al. [7], was used as an adsorbent. Before using, COSAC was washed with distilled water to remove soluble organic matter, dried at 60°C, then grinded and sieved, for a selected particle size range of 0.250-0.500 mm. Specific surface area and pores characteristics of olive stone activated carbon were determined by nitrogen adsorption and desorption isotherms at 77.7 K with an automatic Sorptiometer Autosorb-1C Quantachrome apparatus. The pH_{pzc} and surface functional groups were determined respectively by batch equilibrium technique [8], and Boehm titration [9].

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Adsorption experiments

Equilibrium experiments were conducted on batch mode at temperature of 30 ± 2°C. To obtain the adsorption equilibrium isotherms, a sample of 0.3 g (with particle size range: 0.25-0.5 mm) of COSAC were directly placed into 250 ml glass-stoppered conical flasks containing 50 mL of metal ions solutions having different initial concentrations within the range of 0.2 to 5.0 mM for Pb(II), 0.2 to 8.0 mM for Cd(II) and 0.2 to 14.0 mM for both Cu(II) and Ni(II). The flasks were agitated for 10h with an agitation speed of 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), Cd(II) and Pb(II) on COSAC was undergone in the same conditions as indicated above with an initial metal ions concentration of 1mM and an equilibrium time of 10h. Initial pH solutions were adjusted within the range of 2.0 to 5.5 by adding some volume of 0.1 M NaOH or 0.1M HNO_3.

Adsorption kinetics was investigated at three different initial metal concentrations (0.5, 1 and 1.5 mM) and a fixed adsorbent dose of 6 gL^{-1} COSAC in a batch mixed suspension with 500 mL of metal solution. The temperature of the suspension was maintained at 30 ± 2°C by using a thermostatic bath. Solution samples of 2 mL volume were withdrawn at a pre-set time intervals.

Initial concentrations and final concentrations at equilibrium were measured, after acidification with HNO_3 solution to prevent metal precipitation, by FAAS at the wavelengths 324.8, 232.0, 228.8 nm and 217.0 nm, for Cu(II), Ni(II), Cd(II) and Pb(II), respectively, by using air-acetylene flame.

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

$$q_t = (C_0 - C_t)\frac{V}{m} \quad (1)$$

Where C_0 is the initial metal concentration in the solution (mmol), C_t is the metal concentration remaining in the solution at a given time (mmol), m is the weight of COSAC (g), q_t is the metal ion uptake (mmol.g^{-1}) and V is the volume of solution in the flask.

Linear equation of Langmuir and Freundlich models used to correlate adsorption equilibrium were calculated with Equation (2) and the Equation (3), respectively.

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{\max} K_L}\right) + \left(\frac{1}{q_{\max}}\right) C_e \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (3)$$

where K_L is the equilibrium adsorption constant related to the free energy of the adsorption (l mg^{-1}) and q_{max}: the maximum adsorption capacity (mmol g^{-1}), C_e the equilibrium concentration (mmol l^{-1}), and q_e amount adsorbed at equilibrium (mmol g^{-1}). K_F, (mmol l^{-1})(l g^{-1})$^{(1/n)}$ and n are the constants of Freundlich equation, respectively.

Each experiment was carried out in duplicate and the average results are presented herein.

Results and Discussion

Characterization of activated carbons

The adsorption behaviour of activated carbon is generally determined by the surface area, the pH_{pzc} and by the chemistry of the carbon surface [10]. The specific surface area of COSAC, determined by applying the BET method, was found to be 1086 m^2g^{-1}. The micropores and mesopores volumes were calculated to be respectively 0.51 and 0.01 cm^3g^{-1} (Table 1). This indicates that COSAC is a micropores activated carbon.

Physical properties	
Total area (BET)	1086 $m^2.g^{-1}$
Micropore volume	0.51 cm^3g^{-1}
Total pore volume	0.52 cm^3g^{-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

Table 1: Properties of COSAC.

The pH_{pzc} gives information about the charge of the carbon surface [8], our carbon surface is positively charged at pH values below the pH_{pzc}. In contrast, at solution pH values higher than the pH_{pzc}, negative surface charge increases. COSAC has a pH_{pzc}=3, therefore the carbon surface is negatively charged for pH higher than 3.

Some functional groups occurred on the surface of COSAC (Table1). COSAC contained carboxylic, lactones, phenolic and carbonyl groups, resulting in 4.77 meq.g^{-1} of total acidity. Total basicity of COSAC was 0.75 meqg^{-1}. Results of surface functional groups reported in table 1 indicate the predominance of acidic functional groups, especially carbonyl and phenolic functional groups on the COSAC surface. Physical COSAC properties show a higher specific surface area and developed micropores.

Effect of pH on the adsorption capacity of COSAC

The pH of metal solution is considered to be the most important parameter that can affect the adsorption capacity of activated carbon because of its influence on metal solubility for the dissociation degree of functional groups located on sorbent surface [11,12].

In general, a decrease in ions uptake at acidic pH is due to an increase of competition between hydrogen ions and metal ions for the same adsorption sites. However, an increase in alkalinity enhance metal adsorption rate, due to the predominant presence of hydrated species of heavy metals, changes in surface charge and the precipitation of the appropriate salt. Therefore, there is an optimum pH in which the competition of hydrogen ions is minimized and metal ions precipitation is avoided thus, enhancing metal adsorption.

The experiments were carried out at selected pH values below the pH where metal hydroxide chemical precipitation can occur: pH> 5 for Pb(II) and Cu(II), pH> 6 for $Ni(OH)_2$ and pH>7.8 for $Cd(OH)_2$. These pH values have been retrieved by the chemical species distribution diagrams calculated using the MEDUSA computer program [13].

Figure 1 shows the amount of metal adsorbed and the adsorption percentage of Pb(II), Cd(II), Ni(II) and Cu(II) versus initial solution pH. Results indicate that metal adsorption is strongly pH-dependent and increases with the pH increase until it reaches a maximum at around pH 5. Initially, as the pH of solution was increased from 2.2 to 5.0, the removal percentage of Cu(II), Ni(II), Cd(II) and Pb(II) increased respectively from 16.4 to 62%, from 21 to 78%, from 34 to 97% and from 50 to 100%. The low adsorption at low pH, mainly for

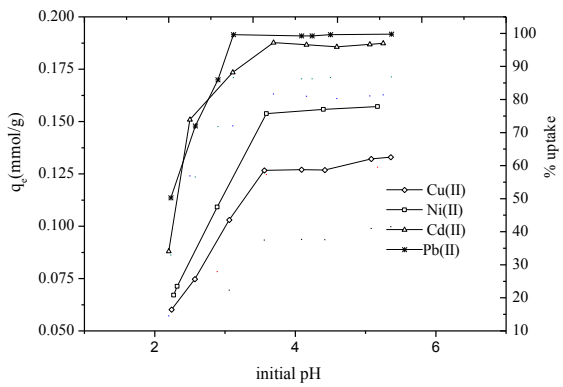

Figure 1: Initial pH effect on the adsorption of metallic ions: Pb(II), Cd(II), Ni(II) and Cu(II).

(C_0: 1mmo/L, equilibrium time: 10h, temperature: 30 °C).

copper and nickel, 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. As said before, COSAC pH_{pzc} was pH 3, therefore, when solution pH is 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. Conversely, for pH > 3, the number of negatively charged sites on COSAC surface increases, and metal adsorption becomes more important.

In most of the reported studies concerning metal ions adsorption onto activated carbon adsorption uptake shows a maximum for initial pH around 5 [14-16].

The important uptake of cadmium and lead even at low pH may be related to higher affinity of the surface functional groups of COSAC for these two metal ions compared to the affinity towards copper and nickel.

Based on these results, the best initial pH for these metallic ions adsorption was considered to be 5 and both kinetics and equilibrium experiments were carried out at this pH.

Adsorption kinetics at different initial concentrations

Equilibrium time: The time necessary to reach equilibrium for copper, nickel and lead adsorption was investigated for different initial concentrations. For these experiments solid-liquid ratio 6 gL^{-1} and pH 5 were kept constant. Results are shown in figure 2. As seen in the figure, the adsorption of Cu(II), Ni(II) and Pb(II) ions onto COSAC increases with time until about 200 min and, thereafter, becomes constant. The adsorption process reaches equilibrium in 270 min for all the studied initial concentrations. With changing the initial concentration of metal ion solution from 0.5 to 1.5 mM, the uptake amounts of Cu(II), Ni(II) and Pb(II) ion increase from 0.061 $mmol.g^{-1}$ to 0.101 $mmol.g^{-1}$, from 0.052 $mmol.g^{-1}$ to 0.090 $mmol.g^{-1}$ and from 0.0701 $mmol.g^{-1}$ to 0.109 $mmol.g^{-1}$, respectively.

From these results, the chosen contact time for further experiments was 10h in order to be sure that equilibrium was achieved.

Kinetics: The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the fluid-solid mass transport process. Kinetic data were submitted to both pseudo-first and pseudo-second kinetic models [17], in order to ascertain which model fitted better to the experimental data.

The pseudo-first order used is that of Lagergren given by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{4}$$

The integration of equation (4) in the conditions (t=0, qt=0) and (t=t, q=qt) gives:

$$Ln(q_e - q_t) = Lnq_e - k_1 t \tag{5}$$

Where k_1 is the velocity constant of the pseudo-first order (min^{-1}).

The pseudo-second order or Ho equation is given by the flowing expression:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{6}$$

By integrating equation (6) into the boundary conditions (t=0, q=0) and (t=t, q=qt), we obtain:

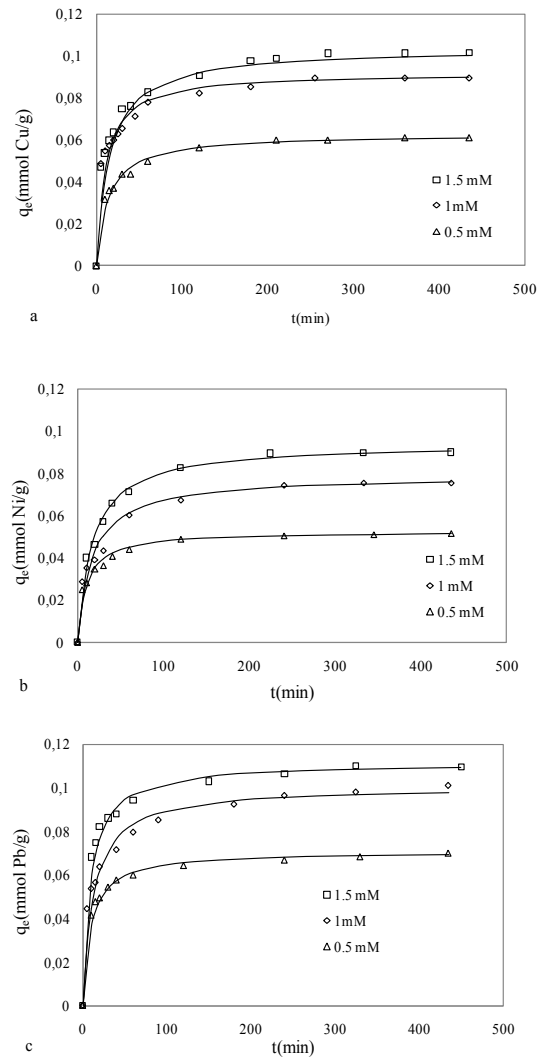

Figure 2: The effect of metal initial concentration on the adsorption of (a): Cu(II); (b): Ni(II); (c): Pb(II), symbols are experimental data and solid lines represent predicted data by pseudo-second- order model, (sorbent concentration:6 gL^{-1}, temperature: 30 °C, pH = 5).

$$\frac{1}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (7)$$

Where k_2 is the velocity constant of the pseudo-second order ($gmmol^{-1}min^{-1}$).

Pseudo-first-order and pseudo-second-order theoretical fitting parameters are listed in table 2. Results showed that the calculated amounts of metal adsorbed ($q_{e,cal}$) by the pseudo-first-order model differ substantially from those measured experimentally, whereas these obtained from the pseudo-second-order kinetic model are very close to experimental data and the correlation coefficient values quite good ($0.985 \leq R^2 \leq 0.999$) and much higher than those find by of pseudo first-order model, suggesting that the adsorbent systems can be well described by the pseudo-second-order kinetic model. Figure 2 illustrates the fit by the pseudo-second-order model of the experimental results of the kinetics of Cu, Ni and Pb adsorption by COSAC.

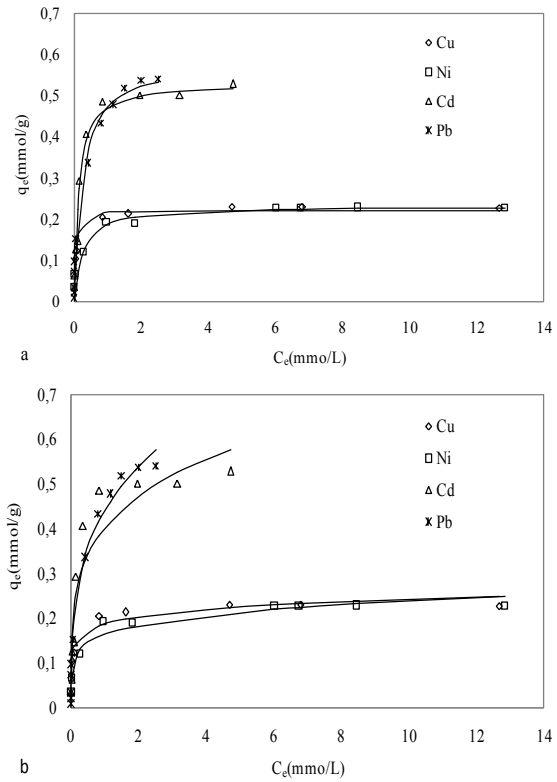

Figure 3: Metal adsorption isotherms on COSAC. COSAC concentration: 6 $g.L^{-1}$; initial pH 5; equilibrium time 10 h; symbols are experimental data and solid lines represent predicted data by Langmuir model (a), and by Freundlich model (b)

Table 2 shows, in one hand, that for all the studied metals, k_2 values decrease with increasing initial concentrations. Thus may be due to the enhancement in the competition between metal cations themselves and between metal cations and H^+ protons for the same active sites. On the other hand, and for the same initial concentration k_2 values found for each metal ion decreased in the following order: Pb(II) >Ni(II) ≥ Cu(II). This indicated that lead was more easily and rapidly adsorbed by COSAC than nickel and copper.

Adsorption isotherms: Equilibrium adsorption studies were performed to determine the maximum metal adsorption capacities of COSAC. Experimental equilibrium isotherms of Pb(II), Cd(II), Ni(II) and Cu (II) ions determined at pH 5.0 and 30°C are showed in figure 3. Isotherms were evaluated using the usually used Langmuir and Freundlich models [18].

Figure 3 shows experimental isotherms data fitted by Langmuir and Freundlich models of the adsorption of Pb(II), Cd(II), Ni(II) andCu(II) metal ions from aqueous solutions on olive stones activated carbon at 30 °C and pH 5. The corresponding Freundlich and Langmuir parameters and correlation coefficients are regrouped in table 3.

Isotherms are of L-type of the Giles classification [19], describing high adsorbate-adsorbent interaction and showing initially a rapid adsorption tending to be asymptotic at higher concentration. Figure 3 also shows that the sites able to bind Pb(II) and Cd(II) are saturated (equilibrium reached) at high metal ions concentrations, as compared to nickel and copper. It is clear that Langmuir model fits to the experimental data very well with high correlation coefficients ($0.98 \leq R^2 \leq 0.999$) as compared to the ones given by Freundlich linear equation ($0.880 \leq R^2 \leq 0.947$). Table 3 also indicates that the theoretical maximum values of adsorption capacity of COSAC given by Langmuir equation (q_{max}) were equal to experimental ones and were found to decrease in the order Pb(II) ≥ Cd(II) > Ni(II) ≥ Cu(II).This trend matches with the order of ionic radius (r_i) of metals and hydration energy but does not match with the values of other characteristics listed in table 4. Pb(II) has the largest ionic radius (1.19A°) followed by those of Cd(II) (0.97A°), Ni(II) (0.72A°) and Cu(II) (0.69A°). For the large non hydrated ions, since the charge is more dispersed, hydration water is held less strongly. 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. The preference of adsorption exhibited for Pb(II) and Cd(II) over Ni(II) and Cu(II) may be also due to the difference hydration energy [20].

Metal	C_0 (mmol)	$q_{e,exp}$ (mmol g^{-1})	Pseudo-first-order			Pseudo-second-order		
			k_1 (min^{-1})	$q_{e,cal}$ ($mmolg^{-1}$)	R^2	k_2 ($g.mmol^{-1}min^{-1}$)	$q_{e,cal}$ ($mmolg^{-1}$)	R^2
Copper	0.5	0.0609	0.013	0.0285	0.968	1.1690	0.0629	0.999
	1	0.0894	0.013	0.0362	0.955	1.0870	0.0917	0.999
	1.5	0.1014	0.017	0.0576	0.946	0.6277	0.1040	0.985
Nickel	0.5	0.0516	0.016	0.0171	0.843	1.4703	0.0527	0.999
	1	0.0756	0.024	0.0414	0.982	0.7514	0.0788	0.999
	1.5	0.0900	0.016	0.0508	0.952	0.6208	0.0942	0.999
Lead	0.5	0.0701	0.002	0.0312	0.947	1.5037	0.0708	0.999
	1	0.1011	0.009	0.0457	0.971	0.7973	0.1009	0.998
	1.5	0.1098	0.01	0.0356	0.968	0.9841	0.1119	0.999

Table 2: Kinetic parameters for the adsorption of Pb(II), Ni(II) and Cu(II) onto COSAC.

Metal ion	q_{exp} (mmol g^{-1})	Langmuir constants			Freundlich constants		
		q_e (mmol g^{-1})	K_L (l $mmol^{-1}$)	R^2	K_F (mmol l^{-1})(l g^{-1})$^{(1/n)}$	n	R^2
Pb(II)	0.5405	0.5417	14.091	0.980	0.4528	2.9069	0.880
Cd(II)	0.5283	0.5327	12.068	0.998	0.4013	3.1545	0.928
Ni(II)	0.2272	0.2306	6.609	0.999	0.1586	5.1282	0.947
Cu(II)	0.2268	0.2290	20.302	0.999	0.1837	7.6923	0.932

Table 3: Calculated Langmuir and Freundlich constants and correlation coefficients for the adsorption of Pb(II), Cd (II), Ni(II) and Cu(II) onto COSAC.

Metal	Ionic radius A°	Hydrated radius A°	Hydration energy (kJmol^{-1})	Solubility of hydroxides (pk_s)	Hydrolysis constants (pK_h)	Electro-negativity
Pb(II)	1.19	4.01	-1481	-	7.80	2.33
Cd(II)	0.97	4.26	-1807	-	11.70	1.69
Ni(II)	0.72	4.04	-2106	14.7	9.40	1.91
Cu(II)	0.69	4.19	-2100	19.6	7.53	2.00

Table 4: Chemical characteristics of the metal ions.

Adsorbent	conditions	Cu(II)	Ni(II)	Cd(II)	Pb(II)	References
Olive stones A.C (ZnCl2)		-	-	1.851	-	Kula et al. 2008
Granular A.C Powdered A.C	pH 5	15.58 26.9		3.37 3.37	15.58 26.90	Faur-Brasquet et al., 2002
Chestnut shell A.C Grapeseed A.C		100.00 48.78	-	-	-	Özc et al. 2009
apricot stone A.C	pH 6.5; 25 °C	24.08	26.9	33.57	22.84	Kobya et al. 2005
hazelnut shell A.C		51.52	-	-	-	Demirbas et al. 2009
hazelnut husks A.C	pH5.7; 18 °C	6.645	-	-	13.05	Imamoglu et al. 2008
Moso bombo A.C S1C1 S2C1 Ma bomboo A.C S1M1 S2M1	 7.54; 25 °C 7.4; 25 °C 10.02; 25°C 7.95; 25°C	 0.401 0.400 0.634 0.398		 0.174 0.257 0.398 0.396	 0.407 0.396 0.404 0.397	Lo et al., 2011
immobilized tannic acid A.C		2.224		1.461		Ucer et al., 2006
Carbon Nanotube	pH 5	28.595		10.903	96.969	Li et al., 2003
Olive stone waste	pH 5	5.655	5.165	16.972	28.386	Fiol et al. 2006
Bamboo activated carbon	pH 5; 23 °C	7.371	6.457	5.170	-	Liu et al., 2005
COSAC	pH 5; 30°C	14.552	13.536	60.021	112.348	In this study

Table 5: Comparison of maximum adsorption capacities (mg.g^{-1}) with various adsorbents for different metal ions.

The affinity constant, K_L, which is related to the adsorbent energy, followed this order: Cu(II) (24.302 l.$mmol^{-1}$) > Pb(II) (14.091 l.$mmol^{-1}$) > Cd(II) (12.068 l.$mmol^{-1}$) > Ni(II) (6.609 l.$mmol^{-1}$). These results indicate that probably not all binding sites on COSAC surface may be available for Cu (II) binding due to its relatively higher hydration energy [20].

The ability of an adsorbent to adsorb heavy metals is reflected in K_F Freundlich constant. The values of this parameter follows the inverse order given by the maximum experimental capacity of COSAC to remove metal ions (Cu(II)>Ni(II)>Cd(II)>Pb(II)). Furthermore, the very high *n* values of the Freundlich model reflect a high affinity between adsorbate and adsorbent and also indicate the existence of chemisorptions process. We can also note either that the highest intensity was obtained for copper adsorption, which highlights the large affinity of COSAC for this metal.

In comparison to other activated carbons studied for the same metal ions adsorption, the adsorption order changes strongly from one adsorbent to another. Ucer et al. [14], found that Cu(II) metal ion was more adsorbed on tannic acid activated carbon than Cd(II) and related the difference to the electronegativity of metal ions. The same tendency was found, for copper and cadmium, by Lo et al. [6], when they studied the adsorption of metal ions onto bamboo activated carbon. The selectivity of adsorption was found to decreases in the order: Pb(II)>Cu(II)>Cd(II). The adsorption capacities order, determined by Faur-Brasquet et al. [16], follow the trend Cu(II)>Ni(II)>Pb(II) on activated carbon cloths, since the activated carbon used is microporous adsorbent, metal ions go through adsorption sites easily when the ionic diameter becomes small. According to this order, Cu(II) must have the small ion diameter than Ni(II) and Pb(II). This is different with our experimental results. These authors explained the differences in adsorption based on the ionic radius, the large ionic radius of Pb(II) compared to that of Cu(II) induces a quick saturation of adsorption sites, because of steric overcrowding thus the surface available for Cu(II) ions is then larger than for Pb(II). The same interpretation was given by Gao et al. [20], when they studied the removal of heavy metal ions on oxidized carbon nanotubes; the uptake amount followed the sequence: Cd(II)>Cu(II)>Ni(II). Whereas the order related to the maximum adsorption of lead, nickel and cadmium onto peanut husks carbon determined by Ricordel et al. [18], was found to be in the order of ionic diameters of the heavy metals used: Pb(II)>Cd(II)>Ni(II). As seen in table 4, lead is the metal with large ionic radius and some authors reported that the adsorption of metals having a larger ionic radius was higher than for those with a smaller ionic radius (Table 3).

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 another (Table 5).

Table 5 lists a comparison of maximum adsorption capacities of different adsorbents towards the metals under study, with data have been collected at different conditions. It can be seen that COSAC has a relatively high adsorption capacities 13.54, 14.55, 60.02 and 112.35 $mg.g^{-1}$ for Ni(II), Cu(II), Cd(II) and Pb(II) ions, respectively. Therefore, COSAC has a significant potential for the removal of these metal ions from aqueous solution.

It can be seen from this table 5 that adsorption amount of metal ions differ from one activated carbon to another and this is partly because of the difference in the functional groups, the specific surface area, pore volume, micropore volume, the average diameter, etc.

For the studied activated carbon, table 1 indicated the dominating of acidic functional groups and the most important compounds are carbonyl groups (2.720 $meq.g^{-1}$), whereas the carboxylic groups present only 0.100 $meq.g^{-1}$.

Many researchers have reported the importance effect of acid functional groups on the adsorption capacity for heavy metal ions [6,21,22]. Kadirvelu et al. [15], indicated that carboxylic groups on adsorbents can play an important role in the adsorption of Cu(II), Pb(II) and Ni(II). Results found by Faur-Brasquet et al. [16], when they studied the removal of Cu(II) and Ni(II) onto three activated carbons; indicated that activated carbon with high carboxylic functions and lower pH_{pzc} is very efficient for copper and nickel metal ions removal.

Lo et al. [6], compared the removal efficiency of two groups of activated carbons; S1M1 and S2C1, based in the difference of the specific surface area, micropore volume and average pore diameter. Results show that for the same group of activated carbons, the adsorption capacity and removal efficiency of heavy metal ions were obtained by carbon that has the large specific surface area, pore volume and micropore area. Nevertheless, these interpretations were not always true when we compare two different groups of activated carbons. When comparing the results showed in table 5, we can conclude that adsorption of heavy metal ions depends on the adsorbent and its preparation by different oxidation agents that influence the surface area, pores distributions, and gives the acidic or basic characteristics of the functions groups formed on the surface of adsorbent. This can be improved by the high difference in the amount adsorption between olive stone waste [23], and the carbon studied derived either from olive stones and oxidised by ortho-phosphoric acid.

Conclusion

The removal of heavy ionic metals from aqueous solution by adsorption on olive stone activated carbon produced by thermo chemical process using phosphoric acid (COSAC) was investigated.

The sorbents adsorption performance was evaluated at different initial pH, contact time and initial ion concentration and the results were discussed on the basis of the sorbent physical and chemical properties. The obtained results show that metal adsorption is pH-dependent and maximum adsorption was found to occur at initial pH 5. Adsorption equilibrium was fast and it was achieved after 4hours for the three different initial concentrations studied. The kinetics of metal adsorption on COSAC follows pseudo-second order rate expression. The equilibrium adsorption data are better fitted by the Langmuir model as compared to Freundlich model and the adsorption capacity of COSAC decreased in the order: Pb(II)≥ Cd(II)>Ni(II)≈ Cu(II). The impregnation with phosphoric acid confers to COSAC characteristics of acidic functional groups (low pH_{pzc}), high surface area and developed micropores. All these features make COSAC a promising sorbent for the removal of heavy metal ion compared to other adsorbents.

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