

Uptake of Cd²⁺ and Ni²⁺ Metal Ions from Aqueous solutions By Activated Carbons Derived from Waste Olive Stones

Th. Bohli, A. Ouederni, N. Fiol, and I. Villaescusa

Abstract—The sorption of heavy metals (Cd²⁺, Ni²⁺) on activated carbons produced from olive stones (OSAC) was studied by using a batch technique. OSAC was prepared by tow processes using phosphoric acid as chemical agent. The physicochemical proprieties of these carbon materials were investigated in the term of N₂ adsorptions, pH_{pzc} and SEM-EDX. Cd(NO₃)₂·4H₂O and Ni(NO₃)₂·3H₂O were used as heavy metal samples. The effects of equilibrium time, initial concentration and initial pH were investigated. The adsorption isotherms of heavy metals from aqueous solution were determined. These isotherms were seen to be consistent with Langmuir adsorption isotherm. The adsorption constant rate was determined for obtained kinetics curves suitable for second degree of rate kinetics. Chemical and combined activated carbons were compared according to their percent of removal of heavy metals.

Index Terms—Olive stones, activated carbon, cadmium, nickel, adsorption, aqueous solution, equilibrium, kinetics adsorption.

I. INTRODUCTION

Environmental pollution by heavy metals has become the most hazard problem since their dangerous effect on aquatic flora and fauna even in relatively low concentrations. Many industrial processes discharge aqueous effluents containing heavy metals such as smelting, metal plating, mining pigments, cadmium-nickel-batteries, brass manufacture [1]. Cadmium and nickel ions are among the most common heavy metal pollutants found and cause harmful and serious problems. Several efforts including the development of chemical processes such as electrofloatation, chemical precipitation, ion exchange, biosorption, co-precipitation/adsorption, flocculation and membrane filtration have been developed to reduce the hazardous effects of toxic metals [2]. Adsorption is considered as the most practical and economical way to remove heavy metals. Activated carbon is still the most important adsorbent in current use in the removal of heavy metal from aqueous solutions due to its large surface area, high adsorption capacity, porous structure, selective adsorption these characteristics depend on the precursor as well in the activated method. Agricultural wastes such as fruit stones;

apricot stone [3], sugar beet pulp[4], tea waste[5], coconut[6], rice husk [7] and pentandra hulls[1] are considered as the major precursor used to prepare activated carbon because they are renewable, available and have a low cost.

Tunisia is classified in the fourth ranking of Mediterranean counties in the production of olive oil. So, olive cultivation constitutes a strategic position within the Tunisian agricultural sector, representing 1, 6 million hectares under cultivation (30% of agricultural land area) and counting an estimated 56 million olive trees.

This high production accompanied obligatory by a big quantity of olive stone waste. The objective of the present work is to investigate the possibility of using olive stone activated carbon prepared by chemical way (COSAC) and combined (MOSAC) way for the removal of heavy metal ions from water. Therefore, experiment of removing Cd(II) and Ni(II), ions from aqueous solution were conducted in batch mode. The effects of contact time, initial solution pH and initial concentration on sorption capacity of COSAC were studied. Kinetic pseudo second order model was used to identify the mechanisms process. Experimental equilibrium data, deduced by sorption isotherm studies, were fitted to the Langmuir and the Freundlich equations in order to decide which model describes better the sorption process.

II. MATERIALS AND METHODS

A. Adsorbent

Olive stone solid used for producing activated carbon are a byproduct from oil factories in southeast Tunisia. Activated carbons from olive stones precursor were prepared according to the two activation process developed in laboratory: a chemical activation (COSAC) where phosphoric acid is used as activation agent and combined activation (MOSAC) the carbon is activated by phosphoric acid and steam water.

The main characteristics of olive stones activated carbons are listed in table 1. Pore characteristics were determined by nitrogen adsorption at 77.7 K with an automatic sorptometer Autosorbe-1 Quantachrome apparatus. Acidic surface functional groups are measured by the Boehm method [8]. The point of zero charge (PZC), i.e., the pH above which the total surface of the carbon is negatively charged below this pH the surface s positively charged and at pH_{pzc}, the value of pH is equal to zero, is also determined[9] .

The surface structure of OSAC is analyzed by scanning electronic microscopy (SEM, Jeol JSM-6400) coupled with energy dispersive X-ray analysis (EDX) (table 1). The results were reported in Fig. 1, SEM of COSAC (Fig. 1a) and MOSAC (Fig. 1b). The internal surface of COSAC (Fig.1a)

Masnucrypt received May 16, 2012; revised July 16, 2012.

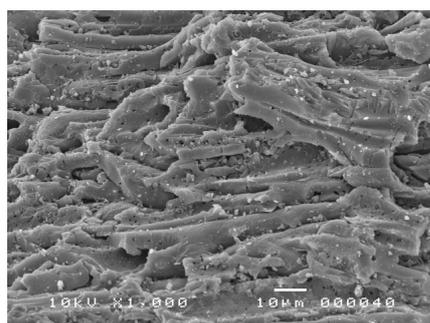
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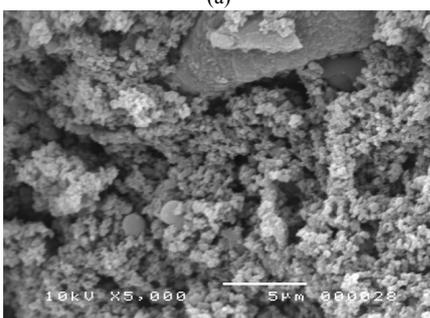
is characterized by the presence of pores of cylindrical form and the outer surface of MOSAC (Fig. 2b) is in the form of nodules.

TABLE I: PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION

Properties	COSAC	MOSAC
Specific surface area BET (m ² /g)	1435	1517
V _{mic} (cm ³ /g)	0,728	0,683
V _{mes} (cm ³ /g)	0,021	0,017
dAP (A°)	19	18,65
pHpzc	3	5
Carbon (%)	87,73	90,11
Nitrogen(%)	1,77	1,34
Oxygen(%)	9,64	7,24
Phosphoric(%)	1,44	0,65
Sulfur (%)	-	0,12



(a)



(b)

Fig. 1. SEM micrographs of (a): COSAC and (b): MOSAC

A. Heavy Metals Solutions

Stock solutions of Cd(II) and Ni(II) are prepared from analytical grade chemicals, Cd(NO₃)₂·4H₂O and Ni(NO₃)₂·12H₂O. Solution of 0.1M NaOH and 0.1M HNO₃ are used for pH adjustment. All working solutions are prepared by diluting the stock solutions with MilliQ-water. Metal standard solutions of 1g/L are used for flame atomic absorption spectroscopy FAAS (VARIAN Absorption Spectrometer (Model A1275)).

B. Adsorption Experiments

Batch mode adsorption experiments are carried out at 28°C using stopper glass tubes of 20 ml capacity by shaking a fixed mass of 0.05g of olive stone activated carbon with 12.5 ml of metal solution. The agitation was realized by a rotary mixer of SBS-ABT4 type. After equilibrium time, solutions are filtrated through 0.45μm cellulose filters paper then final and initial metal concentrations are analyzed by FAAS.

C. Effect of pH

The pH of metal solution is considered as the most

important parameter that can affect the adsorption capacity of activated carbon [10]. This can be due to the fact that hydrogen ions themselves are strong competing sorbate and the solution pH influences the chemical speciation of metal ions as well as the ionization of function groups onto sorbent surfaces [11].

In order to evaluate the influence of this parameter, experiments were carried out at different initial pH values. The pH ranges are chosen from 2 to 8 for cadmium and from 2 to 6.5 for nickel in order to avoid precipitation of metal hydroxides, which has been estimated to occur at pH>7 for Ni(OH)₂(s) and pH> 9 for Cd(OH)₂(s) as can be observed in speciation diagram plotted by Medusa program (Fig. 2).

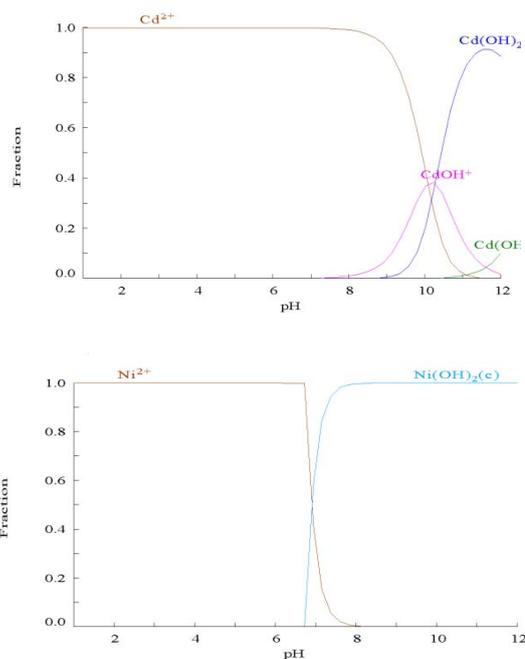


Fig. 2. Speciation diagram for Cd(II) and Ni(II); C=1 mmol/l.

B. Adsorption Isotherms

The equilibrium isotherm of heavy metal ions between solid adsorbent and the solution is important to determinate the maximum sorption capacity. Langmuir and Freundlich models are used to describe the equilibrium sorption. Langmuir isotherm model suppose that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir equation expressed as:

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

where q_e (mmol/g) is the amount of metal adsorbed per specific amount of adsorbent, C_e (mmol/l) is the equilibrium concentration of the solution, q_{max} (mmol/g) is the maximum amount of metal ions required to form a monolayer. K_L is the Langmuir constants.

Freundlich model is based on sorption on heterogeneous surfaces and does not provide any information on the monolayer adsorption capacity. Freundlich equation is commonly represented by:

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

Where K_F and n are the Freundlich constants indicate respectively adsorption capacity and adsorption intensity [12].

III. RESULTS AND DISCUSSION

A. Equilibrium Contact Time

Results of kinetic experiments are shown in Fig. 3. Cd(II) and Ni(II) metal ions, with the same initial molar concentration (0,8 mmol), had very similar kinetic adsorption. For both heavy metal ions, adsorption kinetic rate is very rapid and adsorption equilibrium was reached at approximately 30 min. The very fast sorption kinetics observed with COSAC represents an advantageous aspect for a continuous-flow water treatment system.

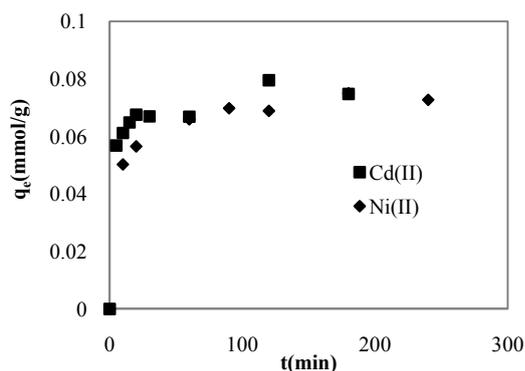


Fig. 3. Effect of contact time on the adsorption of Cd(II) and Ni(II) on COSAC ($C_0 = 0,8$ mmol/L, $T = 28^\circ\text{C}$, $m_{CA} = 4\text{g/l}$).

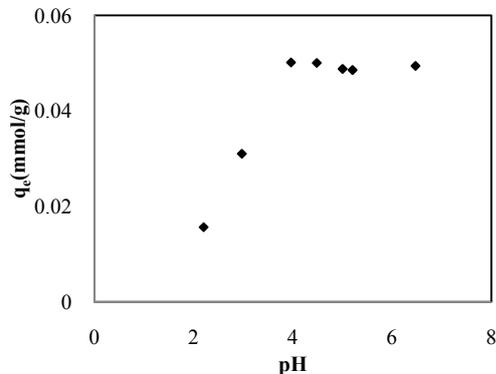


Fig. 4. Effect of initial pH on the adsorption of Ni(II) on COSAC ($C_0 = 0,351$ mmol/L, $\text{pH} = 4,5$, $T = 28^\circ\text{C}$, $m_{CA} = 4\text{g/l}$).

B. Effect of Initial pH

Fig. 4 shows the amount of metal ion adsorption for Cd(II) and Ni(II) on activated carbon as function of pH. Results indicate that metal adsorption depend strongly with pH and increased with increasing pH. This increase in metal ions removal with pH may be due to the decrease in electrostatic repulsion between cations and the positively charged surface of COSAC at $\text{pH} > \text{pH}_{PZC}$ ($\text{pH}_{PZC} = 3$). Below pH_{PZC} , the surface is positively charged under these conditions the uptake of metal ions would be quite low due to electrostatic repulsion, beyond pH_{PZC} the negative charge on the surface of adsorbent increase thereby enhancing the metal adsorption. For all experiments, pH 4.5 was chosen as the optimum solution pH.

C. Influence of Initial Metal Ions Concentration on Removal Efficiency

It was observed from Fig. 5 that the amount of Cd(II) adsorbed increased from 0.0784 to 0.0974 mmol/g with an increase in the initial metal ions concentration in solution from 0,77 to 1,5 mmol/L.

Also the removal of Ni(II) is affected by the initial concentration, with increasing of initial concentration from 0,77 to 1.2 mg/L the adsorption uptake increases from 0.0688 to 0.0963 mmol/L. These effects can be explained as follow: At lower concentration, the number of metal ions which are available in the solution is less as compared to the available sites on the adsorbent. However, at higher concentration the available sites for adsorption become fewer and the adsorption amount of metal ions depends on the initial concentration. Fig. 5 shows also that cadmium and nickel metal ions have the some affinity to COSAC. For the some initial concentration the same amount quantity is found for both metal ions.

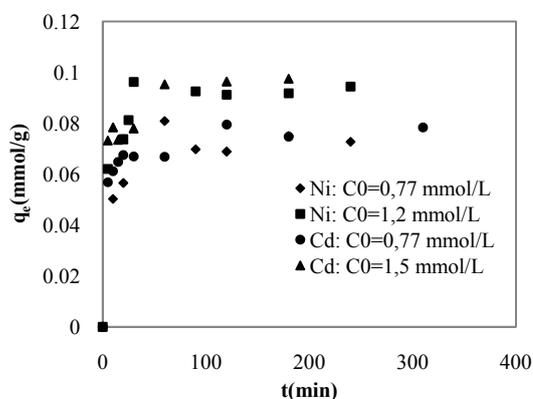


Fig. 5. Effect of initial metal ions concentration on removal efficiency of Cd(II) and Ni(II) on COSAC ($\text{pH} = 4,5$, $T = 28^\circ\text{C}$, $m_{CA} = 4\text{g/l}$).

Adsorption equilibrium studies are important to determinate the efficiency of adsorption. In spite of this, it is also necessary to identify the adsorption process in a given system. Adsorption kinetics was expressed as the solute removals rate that control the resistance time of the sorbate in the solid-solution interface. Adsorption process depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. Kinetic adsorption data of Cd(II) and Ni(II) adsorption by COSAC are fitted by the pseudo second order kinetics model. This model is given by the equation below:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3)$$

Integration of (3) and rearrangement of the resultant equation gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k is the rate constant, q_e is the equilibrium metal uptake and q_t is the metal uptake at a given time t .

The rate constant, k , and the equilibrium metal uptake, q_e , can be obtained from the plot of t/q_t versus t as shown in Fig. 6.

The q_e and the k_2 values for the pseudo-second-order models are also shown in Table III. It may be seen that the sorption kinetics can be satisfactorily and adequately represented by the pseudo-second-order model using non-linear regression fit, as indicated by regression coefficient values, R^2 , close the unity for all cases. From Table II, it is observed that the q_e values increase with an increase in C_0 , whereas, k_2 decreases with an increase in C_0 . For the same initial concentration k_2 value of $Cd(II)$ is less than for $Ni(II)$, this can indicate that the kinetic rate cadmium adsorption is faster than for $Ni(II)$.

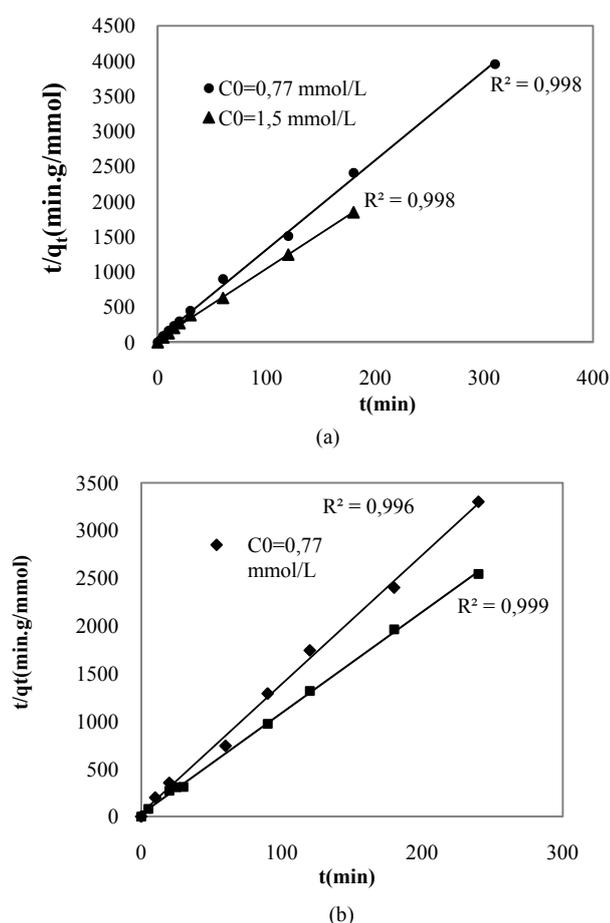


Fig. 6. Pseudo-second order kinetics of adsorption of (a):Cd(II) and (b): Ni(II)on COSAC(pH 4.5, mCA= 4 g/l , 28°C)

TABLE II: PSEUDO-SECOND ORDER KINETIC MODEL PARAMETERS

	C_0 (mmol/L)	K_2 (g.min-1mmol-1)	q_e (mmol/g)	R^2
Cd(II):	0.77	3.627	0.078	0.998
	1.5	2.656	0.099	0.998
Ni(II):	0.77	5.005	0.074	0.996
	1.2	4.222	0.094	0.999

A. Batch Mode Adsorption of Metal Ions on Cosac and Mosac

Equilibrium sorption studies are performed to provide the maximum metal adsorption capacities of OSAC. Adsorption isotherms of nickel on COSAC and MOSAC ($dp < 0.125$ mm) are presented in Fig. 7. A commercial activated carbon supplied by Chemviron is used in the aim of a comparison and valuation of synthetic olive stone activated carbon in

sorption capacities of heavy metals. It can be observed that the adsorption capacities q_{max} (Table III) order following: MOSAC \geq COSAC $>$ Chemv. In spite of the difference in functional surface groups, MOSAC and COSAC have the some affinity to remove nickel.

Adsorption capacity of COSAC in cadmium and nickel metal ions elimination is given by Fig. 7. This figure shows that there is no difference between adsorption of cadmium or nickel on COSAC.

The equilibrium isotherms were modeled using Langmuir and Freundlich models. Freundlich isotherm constants K_F and n are determined from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$. The slope and intercept of plots of C_e/q_e versus C_e were used to calculate q_{max} and K_L . All these parameters were given in Table III.

The simulated curves determined using Langmuir and Freundlich models, plotted by Solver-Excel program, were given in Fig. 8. Langmuir isotherm fits better the experimental data than Freundlich model and this result can be observed from Fig. 8 and 9. The correlation coefficients (R^2) values indicated that Langmuir model describe adequately the sorption isotherm of cadmium and nickel on olive stones activated carbon prepared by chemical and combine way. The values of maximum uptakes given by Langmuir models are in good agreements with experimental capacities calculated from isotherms. Then, the values of n of Freundlich model, which reflect the intensity of adsorption, are greater than unity, indicating that heavy metal ions are favorably adsorbed on OSAC. Isotherms with $n > 1$ are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and are indicative of chemisorptions [13], [14]. In this study n values (Table III) are all greater than unity indicating chemisorptions.

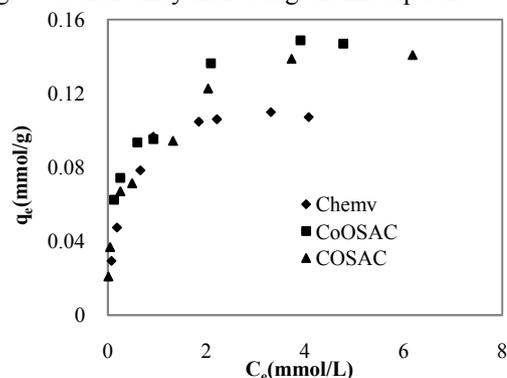


Fig. 7. Comparison of adsorption isotherms of Ni(II) removal (pH 4.5, mCA.4 g/l, C_0 : 0,01-6 mmol/L, T=28°C).

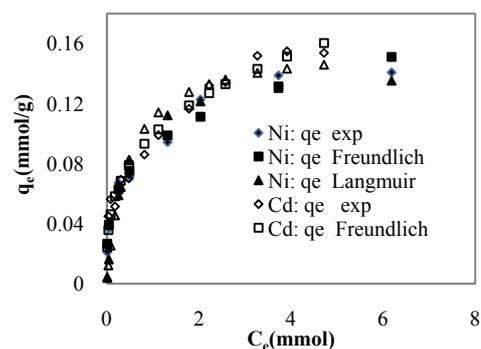


Fig. 8. Comparison of the various adsorption isotherms for metal ions removal on COSAC (pH 4.5, mCA. 4 g/l, C_0 : 0,01-6 mmol/L, T=28°C)

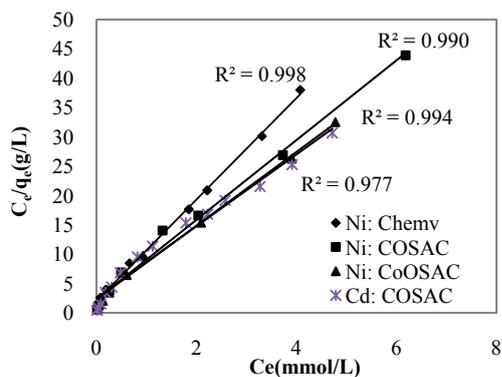


Fig. 9. Langmuir isotherm plots for the adsorption of Cd(II) and Ni(II) on activated carbons

TABLE III: ISOTHERM MODEL PARAMETERS FOR THE THREE MEAL IONS ADSORPTION

Model	Cd(II)		Ni(II)		
	COSAC	COSAC	MOSAC	Chemv	
Freundlich	K_F	0.099	0.091	0.104	0.075
	n	3.228	3.625	4.058	2.230
	R^2	0.970	0.985	0.979	0.925
Langmuir	K_L	2.227	2.732	3.411	3.812
	q_{max}	0.159	0.143	0.151	0.117
	R^2	0.977	0.990	0.994	0.998

IV. CONCLUSION

This study indicated that activated carbon prepared from olive stone with chemical and combined process with phosphoric acid can be used as an effective adsorbent material for the treatment of Cd(II) and Ni(II) metal ions from aqueous solutions as compared by a commercial one. The adsorption of cadmium and nickel on activated carbon was found to be time, initial concentration and initial pH. It was found that the a

dsorptive uptake of metal ions was very fast and the maximum sorption for both Cd(II) and Ni(II) metals ions was found to occur at pH around 4.5.

It was also observed that there is no difference between metal ions uptake on COSAC and on MOSAC. Equilibrium

results show that the sorption of both metal ions from aqueous solutions can be predicted reasonably well by Langmuir model. Pseudo second order kinetic model fit correctly the kinetics experimental data.

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