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RESEARCH ARTICLE

COPPER BIOSORPTION ON ARGAN NUT SHELL: KINETIC AND THERMODYNAMIC STUDIES.

Youssef El Boundati[1], Khadija Ziat[1], Ahmed Naji[2], Mohamed Saidi[1] and Lotfi Rghioui[3].

1. Laboratory Physico-Chemistry of Materials, Natural Substances and Environment, Department of Chemistry, Faculty of Sciences and Techniques, Abdelmalek Essaâdi University, Tangier (Morocco).
2. Laboratory of Mathematics and Applications, Mathematics Department, Faculty of Sciences and Techniques, Abdelmalek Essaâdi University, Tangier (Morocco).
3. Laboratoire de Spectroscopie, Modélisation Moléculaire, Matériaux et Environnement (LS3ME), Faculty of Sciences, Mohammed V-Agdal University, Rabat (Morocco).

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Abstract

This work studies the adsorption of copper from aqueous solutions using Argan nut shell (ArNS) powders. ArNS was characterized by different techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and BET. The fractal-like kinetic models, and their classical counterparts, have been used to describe the kinetic adsorption of copper on ArNS. The modeling results show that the fractal-like kinetic models fit properly the kinetic data in comparison with the classical models. Thermodynamic quantities, such as Gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy change of sorption (ΔS°) have also been evaluated and it has been found that the sorption process was feasible, spontaneous and endothermic in nature. The reported findings indicate that Argan nut shell could be employed as a low-cost alternative adsorbent for efficient removal of copper ions from aqueous solutions.

Introduction: -

Removal of pollutants from industrial wastewater, especially heavy metals, has become one of the most important issues due to the increase in industrial activities. Copper is one of the most toxic heavy metals to living organisms and one of the most widespread heavy metals in the environment [1]. Numerous efforts have been undertaken to find effective and low cost methods to remove copper from waste solutions. Adsorption is one of the most popular methods for the removal of heavy metals from the wastewater [2]. Recently, several kinds of low cost adsorbents have been investigated for the removal of copper, including agricultural and industrial solid wastes [3–5].

The accurate description of a liquid-solid adsorption unit requires adequate mathematical expressions, for both adsorption equilibrium and kinetics, in order to establish the nature of pollutant sorbent interactions. There are several models of adsorption kinetics for homogeneous and heterogeneous systems. Pseudo-first order (PFO) [6] and pseudo-second order (PSO) [7] models are the most frequently used to analyze the adsorption kinetic data. These models assume time-invariant kinetic constants. In this framework, Koppelman showed that classical reaction kinetics (constant kinetic parameters) are not applicable for heterogeneous diffusion-limited processes, where the reactants are spatially constrained by walls, phase boundaries or force fields such as in porous solids [8].

Corresponding Author:-Khadija Ziat.
Address:-Laboratory Physico-Chemistry of Materials, Natural Substances and Environment, Department of Chemistry, Faculty of Sciences and Techniques, Abdelmalek Essaâdi University,

In the present study, the biosorption characteristics of Argan nut shell for copper were investigated. The adsorption kinetic was examined by applying the pseudo-first order and the pseudo-second order models in their classical and fractal forms. The thermodynamic parameters related with the process were also evaluated and reported.

Materials and methods

Characterization

The chemical composition of ArNS was determined by means of X-ray fluorescence using an Axios Spectrometer. X'Pert Pro was used to investigate the mineralogical composition of the ArNS samples. X-ray diffraction for the materials was measured using CuKα radiation at 45 kV and 40 mA over the range of 3° to 90° (2θ) at a scan speed of 0.067°/min. To identify the functional groups of ArNS, Fourier transform infrared spectroscopy analysis was conducted on a FTIR spectrophotometer (Vertex 70) with the absorption spectrum between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The FTIR spectra were analyzed and compared before and after loading with copper. The surface analysis of ArNS was carried out by BET method using a Quantachrome Autosorb automated nitrogen adsorption system at 77 K.

Adsorbent and adsorption experiments

Argan nut shells were obtained from a specific tree in Morocco (Argania Spinosa). ArNS was washed with bi-distillated water to remove soluble impurities until the water turned clear, then dried at 378 K for more than 24 hours. Finally, the samples were crushed with a grinder and then sieved to a particle size smaller than 100 µm.

The adsorption kinetics experiments of ArNS were carried out, as in the equilibrium studies, by adding 10 g/L of sorbent to 25 mL of 150, 250, 350 and 450 mg/L of copper solution prepared by dissolving the appropriate amount of copper salt ($CuSO_4.5H_2O$) (analytical reagent grade, Riedel-de Haën) in bi-distillated water, at different temperatures 288, 298, 308 and 318 K, in appropriate time intervals from 5 to 240 min. The mixtures were agitated with a shaker (WTW OxiTop IS 6) placed in an incubator (Refrigerated Incubators FTD I.S. Co.) to ensure the desired temperature. The pH of solutions was adjusted by HCl (analytical reagent grade, Riedel-de Haën) 0.1 M or NaOH (analytical reagent grade, Fluka) 0.1 M. The copper concentration in liquid phase was analyzed by means of atomic absorption spectrophotometry using a spectrophotometer (Jobin Yvon 2). The adsorption capacity of the adsorbent was calculated as follows [9]

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

where q_t is the adsorption amount at the time t (mg/g); C_i and C_t are the solute concentrations in the bulk solution initially and at the time t (mg/L) respectively; V is the volume of the solution (L) and m is the mass of the adsorbent (g).

Mathematical modelling of kinetic data

Data of kinetic experiments of biosorption of copper on ArNS were modeled using the pseudo-first order, (Eq. (2)) and the pseudo-second order, (Eq. (3)) models

$$q_t = q_e\left(1 - exp\left(-k_1 t\right)\right) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where q_e is the adsorbed amount at equilibrium (mg/g), k_1 is the pseudo-first order rate constant of sorption (min^{-1}) and k_2 is the pseudo-second order rate constant of sorption [g/(mg.min)].

Kopelman introduced the following equation to express the rate coefficient that exhibited temporal "memories" [8]

$$k_f = k' t^{-h} \quad (4)$$

where k_f is the instantaneous rate coefficient, k' is the time-independent rate coefficient and h is the fractal exponent. This parameter determines the fractal behavior [10].

The fractal-like pseudo-first order model (f-PFO) and the fractal-like pseudo-second order model (f-PSO) are as follows [11]

$$q_t = q_e\left[1 - \exp\left(-\frac{k_1'}{1-h} t^{1-h}\right)\right] \quad (5)$$

$$q_t = \frac{\frac{k_2'}{1-h} q_e^2 t^{1-h}}{1+\frac{k_2'}{1-h} q_e t^{1-h}} \quad (6)$$

where k'_1 and k'_2 are the kinetic constants for the f-PFO and f-PSO models, respectively. Eqs. (5) and (6) were applied to adsorption kinetic data of ArNS–Cu system.

The adsorption half-time, $t_{0.5}$, is the time necessary to adsorb half of the equilibrium quantity [12]. It can be calculated by setting the fractional uptake, q_t/q_e, to one half.

Temperature dependence of kinetic data can be determined by using Arrhenius absolute rate theory [13]

$$k(T) = A exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

$$lnk(T) = ln A - \frac{E_a}{RT} \quad (8)$$

where E_a is the activation energy, R, the gas constant, T, temperature, and A, pre-exponential factor related to the frequency of collisions.

Kinetic experiments data have been optimized by using non-linear least-squares fitting method. Three error functions, such as the coefficient of determination R^2, the sum of squares errors SSE and the sum of absolute errors SAE were applied to confirm the experimental data and the best fitting model equation [14]

$$R^2 = \frac{\sum_{i=1}^{n}\left(q_{t,exp} - \overline{q_{t,cal}}\right)^2}{\sum_{i=1}^{n}\left(q_{t,exp} - \overline{q_{t,cal}}\right)^2 + \sum_{i=1}^{n}\left(q_{t,exp} - q_{t,cal}\right)^2} \quad (9)$$

$$SSE = \sum_{i=1}^{n}\left(q_{t,exp} - q_{t,cal}\right)_i^2 \quad (10)$$

$$SAE = \sum_{i=1}^{n}\left|q_{t,exp} - q_{t,cal}\right|_i \quad (11)$$

Thermodynamic parameters

To evaluate the influence of temperature on the adsorption process, the changes in enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were considered. ΔH° and ΔS° can be calculated from the slope and intercept of the straight line obtained by plotting lnk_d versus 1/T, respectively using the following equation [15,16]

$$ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$k_d = \frac{\left(C_i - C_e\right)}{C_e} \times \frac{V}{m} \quad (13)$$

$$\Delta G^\circ = -RT\, ln\, k_d \quad (14)$$

Results and discussion:-

Biosorbent characterization

The chemical composition indicates that carbon (27 %) and oxygen (73 %) are the main elements of the biosorbent. The BET surface area, the pore volume and the bulk density of the Argan nut shell were 10 m^2/g, 0.0084 cm^3/g and 0.808 g/cm^3, respectively. The X-ray diffractograms of ArNS and ArNS–Cu are presented in Figure 1. The diffractograms present a broad peak at around 2θ = 22° and show the strong amorphous biosorbent characteristics existing in the ArNS.

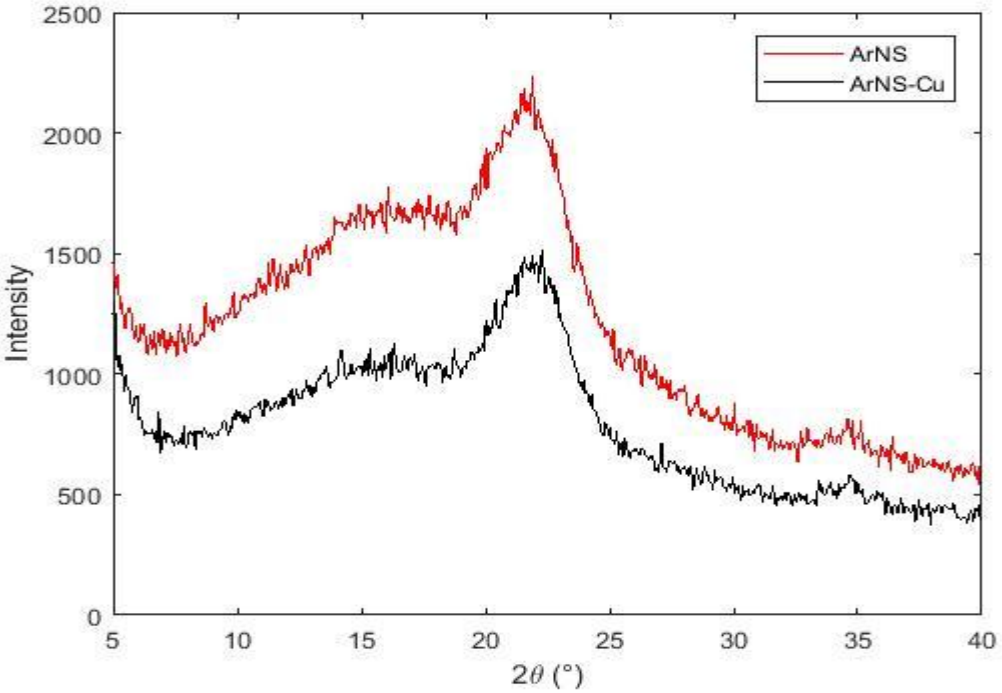

Figure 1: -XRD patterns of ArNS and ArNS–Cu.

Argan nut shell is composed of cellulose ($C_6H_{10}O_5$) and carbohydrate ($C_nH_{2n}O_n$). Organic functions are alcohol and aldehyde or ketone and ether. FTIR spectra of before and after copper biosorption are illustrated in Figure 2. The band assignments are given in Table 1. The pronounced broad band located at 3335 cm^{-1} and the one at 3269 cm^{-1} are attributed to the O–H stretching vibration of alcohol and adsorbed water [4,17,18]. Their bending vibrations are located at 1635 and 1594 cm^{-1} for adsorbed water and between 1375 and 1246 cm^{-1} for alcohol function [19,20]. The aldehyde function of carbohydrate corresponds to the intense vibration shown at 1733 cm^{-1} [17]. Both bands between 2940 and 2874 cm^{-1} are attributed to the C–H stretching vibrations, while the C–H in-plane bending vibrations cause the bands at 1464 and 1424 cm^{-1} [21,22]. The band at 1036 cm^{-1} is due to the mode of the C–O stretching vibration of the ether and alcohol functions [4,22,23]. The infrared spectrum of the Argan nut shell, after the adsorption of copper, is identical to the Argan nut shell before adsorption, except the large shift (11 cm^{-1}) of the band due to the vibration of the O–H bond. This suggests that the bond O–H is involved in the adsorption process. Similar results were obtained for copper adsorption on other sorbent [24].

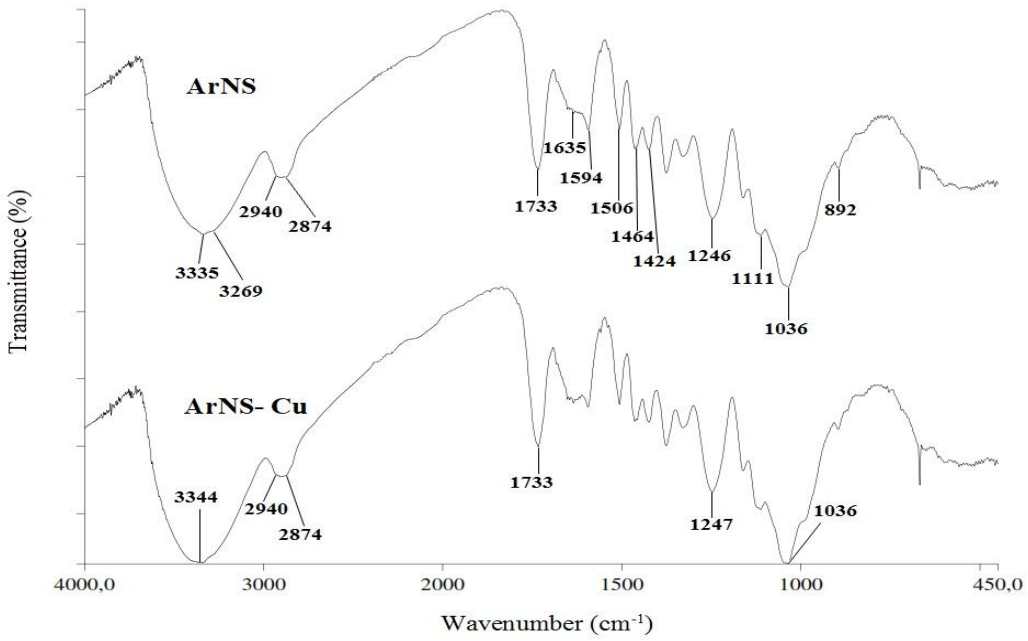

Figure 2: -Infrared spectra of ArNS and ArNS–Cu.

Table 1: -Infrared wavenumbers of Argan nut shell vibrations (cm^{-1}) and their attributions.

ArNS	ArNS–Cu	Functional group assignment
3335	3344	ν(O–H)
2900 2874	2903 2874	ν(C–H)
1733	1733	ν(C=O)
1635 1594	1635 1594	δ(O–H) (water)
1506	1506	ν(C–C)
1464 1424	1464 1424	δ(C–H)
1376 1330 1246	1376 1329 1247	δ(O–H) (alcohol)
1161 1111 1036 985 892 867 829	1161 1113 1036 985 892 867 829	ν(C–O) + ν(C–O–C) (cyclic) + δ(C–O–H) and γ(C–H)

Adsorption kinetics and thermodynamics

Table 2 reports the main kinetic parameters best-derived as best-fitting constants from the application of the Eqs. (2), (3), (5) and (6) to experimental data of copper biosorption on ArNS. The comparison between the two classical models shows that pseudo-second order model gives the best fit of adsorption kinetic for ArNS–Cu. On the

other hand, each fractal kinetic model determines a more reliable adsorption prediction when compared to its classical formulation, as confirmed by the lower values of the error functions. Among fractal-like kinetics, the fractal-like pseudo-first order is the most suitable model to describe copper biosorption in all the experimental conditions. Increasing the temperature or initial concentration of adsorbate leads to the increment of kinetic constants. The fractal exponent h increases by increasing the initial concentration of solute. These results are consistent with those reported in literature for other adsorption kinetic systems [11,25]. The rise of temperature leads to the decrease in h. Similar observations were reported by Marczewski et al. [26].

Table 2: -Adsorption kinetic parameters for adsorption of copper onto ArNS.

		PFO						PSO						f-PFO							f-PSO						
T (K)	C_i(mg/L)	q_e	k_1	$t_{0.5}$	$1-R^2$	SSE	SAE	q_e	k_2	$t_{0.5}$	$1-R^2$	SSE	SAE	q_e	k'_1	h	$t_{0.5}$	$1-R^2$	SSE	SAE	q_e	k'_2	h	$t_{0.5}$	$1-R^2$	SSE	SAE
45	150	6.044	0.215	3.227	0.00284	0.09115	0.69315	6.289	0.064	2.499	0.00380	0.12217	0.78151	6.090	0.245	0.244	2.737	0.00130	0.04158	0.45646	6.289	0.064	0.000	2.499	0.00380	0.12217	0.78151
	250	7.420	0.183	3.794	0.01367	0.67740	1.50570	7.773	0.041	3.113	0.00411	0.20181	0.87007	7.579	0.223	0.393	2.844	0.00249	0.12180	0.65713	7.773	0.041	0.000	3.113	0.00411	0.20181	0.87007
	350	8.944	0.246	2.814	0.02440	1.76450	3.12750	9.356	0.045	2.354	0.00441	0.31239	1.29860	9.465	0.239	0.631	1.206	0.00124	0.08780	0.61674	9.831	0.046	0.359	1.719	0.00171	0.12069	0.75537
	450	9.254	0.265	2.611	0.00274	0.20338	1.06830	9.560	0.057	1.833	0.00140	0.10398	0.65593	9.352	0.305	0.374	1.761	0.00074	0.05468	0.55923	9.560	0.057	0.000	1.833	0.00140	0.10398	0.65593
35	150	5.644	0.092	7.518	0.03312	1.02910	1.92040	6.004	0.025	6.588	0.02264	0.69566	1.62120	5.768	0.136	0.332	6.273	0.01888	0.56710	1.39710	6.039	0.026	0.035	6.591	0.02257	0.69353	1.63410
	250	6.830	0.146	4.733	0.02347	1.01240	2.19200	7.222	0.033	4.153	0.00338	0.14307	0.73888	7.061	0.195	0.436	3.418	0.00105	0.04420	0.47504	7.251	0.036	0.032	3.920	0.00110	0.04650	0.45583
	350	8.481	0.179	3.867	0.03155	2.11110	3.49760	8.979	0.031	3.550	0.00415	0.26992	1.27480	9.136	0.195	0.601	2.406	0.00014	0.00935	0.18876	9.619	0.032	0.357	3.191	0.00008	0.00548	0.15976
	450	8.531	0.193	3.600	0.03179	2.14470	3.50240	9.015	0.034	3.278	0.00470	0.30839	1.38280	9.222	0.199	0.621	2.068	0.00007	0.00475	0.15397	9.728	0.033	0.392	2.826	0.00011	0.00706	0.16742
25	150	5.314	0.071	9.780	0.04232	1.17590	2.22530	5.712	0.020	8.910	0.01474	0.39779	1.19820	5.647	0.119	0.454	8.337	0.00616	0.16374	0.83186	6.253	0.021	0.290	10.534	0.00868	0.23276	1.06050
	250	6.451	0.076	9.159	0.04863	1.99220	2.68610	6.900	0.018	8.089	0.02157	0.85827	1.66950	6.825	0.127	0.462	7.442	0.01265	0.49244	1.39940	7.543	0.019	0.301	9.357	0.01531	0.60543	1.64520
	350	7.747	0.101	6.876	0.05438	3.17920	3.77810	8.254	0.020	6.053	0.01679	0.94348	1.99070	8.395	0.148	0.544	5.312	0.00638	0.35245	1.19490	9.267	0.020	0.388	7.099	0.00780	0.43444	1.33420
	450	7.946	0.113	6.144	0.03692	2.22600	3.41700	8.467	0.021	5.548	0.00704	0.41161	1.16900	8.444	0.159	0.506	4.753	0.00256	0.14866	0.81781	9.008	0.023	0.274	5.728	0.00324	0.18859	0.87899
15	150	4.704	0.068	10.247	0.06989	1.57410	2.79960	5.077	0.021	9.477	0.03073	0.66313	1.74710	5.647	0.103	0.594	11.892	0.01017	0.21260	1.00140	6.922	0.015	0.528	25.724	0.01061	0.22436	1.03550
	250	5.986	0.042	16.406	0.05995	2.19640	2.60530	6.575	0.010	15.993	0.03528	1.25620	2.19090	6.797	0.082	0.483	17.445	0.01656	0.56840	1.77800	8.654	0.009	0.440	37.159	0.01868	0.65364	1.93440
	350	7.172	0.051	13.559	0.05982	3.11980	3.35970	7.813	0.010	12.878	0.02622	1.31780	2.32880	8.310	0.091	0.527	14.955	0.00695	0.34011	1.42470	10.000	0.009	0.443	26.929	0.00834	0.41135	1.56700
	450	7.327	0.064	10.796	0.04317	2.30740	2.83190	7.914	0.013	10.045	0.01422	0.73684	1.76650	7.845	0.110	0.452	9.625	0.00550	0.28072	1.11860	8.771	0.014	0.298	12.520	0.00760	0.39133	1.40500

Also, from Table 2, it can be seen that the adsorption half-time decreases by increasing the temperature, or the initial concentration of adsorbate. This indicates that $t_{0.5}$ depends on the reaction conditions. By using the Eq. (8), the activation energy, E_a, is calculated from the slope of the linear plot lnk(T) versus 1/T (Figure not shown). The value of E_a was 22.34 kJ/mol for the fractal-like pseudo-first order model. Figure 3 represents the predicted adsorbed amount as a function of time based on Eqs. (2), (3), (5) and (6). From this figure, it is within sight, that the increase of the initial concentration of adsorbate or temperature, leads to the increment of adsorbed amount and the rate of adsorption. This was due to the increase in the driving force for mass transfer, which is the concentration gradient [27]. The increase of q_t with temperature can be attributed to the enlargement of pore size [28].

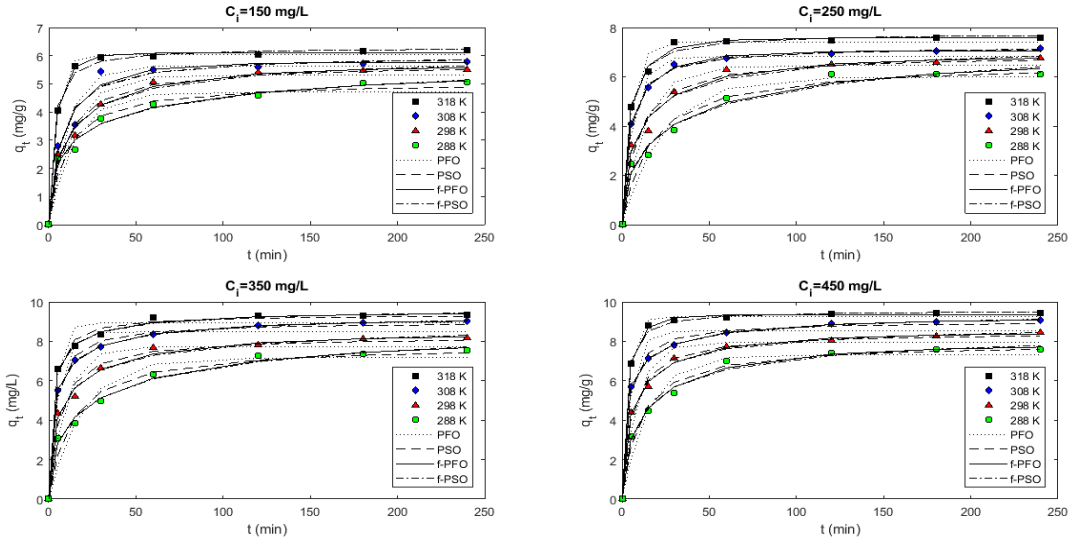

Figure 3: -Adsorption profiles of copper adsorption on ArNS at various temperatures and initial concentrations of solute. Comparison between experimental data (symbols) and by fitting with PFO (Dotted line), PSO (Dashed line), f-PFO (solid lines) and f-PFO (Dash-dotted line) kinetic models.

For further investigation, the variation of instantaneous adsorption rate coefficient, k_f , with time, for ArNS–Cu, based on Eqs. (4) and (5), has been plotted in Figure 4. This figure shows that k_f is not a constant parameter, it depends on the time suggesting a fractal-like kinetic. In addition, k_f decreases as the time increases.

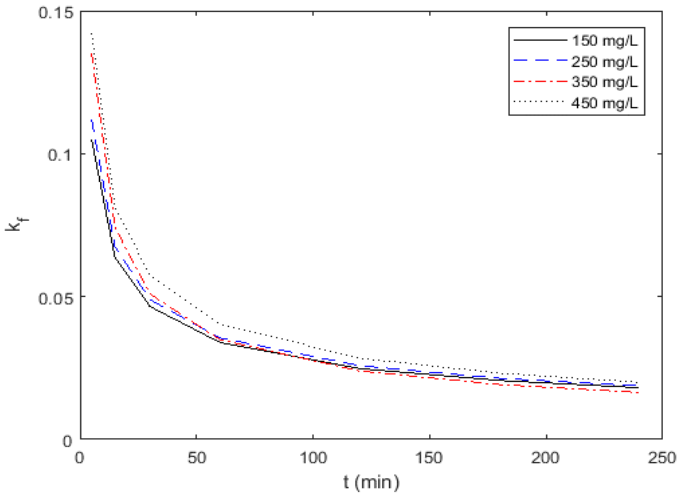

Figure 4: -Time evolution of the fractal-like pseudo-first order instantaneous rate coefficient for copper biosorption on ArNS.

Figure 5 illustrates the dependence of logarithm of k_d on 1/T. The obtained plots are linear, allowing to estimate ΔH° and ΔS° by using Eq. (12). Furthermore, the standard Gibbs free energy at different temperatures and the initial concentrations of solute were calculated based on Eq. (14). The results are listed in Table 3.

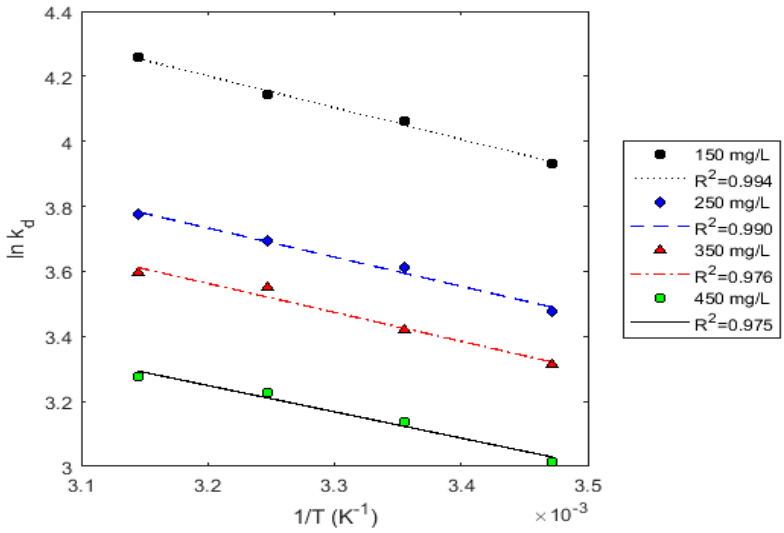

Figure 5: The dependence of logarithm of k_d on 1/T coefficient for copper biosorption on ArNS.

Table 3: *Thermodynamic parameters of copper biosorption on Argan nut shell.*

C_i (mg/L)	T (K)	k_d (mL/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)	R^2
150	318	70.660	-11.257	8.081	60.786	0.994
	308	63.037	-10.611			
	298	58.160	-10.067			
	288	50.965	-9.413			
250	318	43.621	-9.982	7.545	54.893	0.990
	308	40.183	-9.458			
	298	36.991	-8.946			
	288	32.386	-8.327			
350	318	36.388	-9.503	7.391	53.273	0.976
	308	34.796	-9.089			
	298	30.555	-8.472			
	288	27.525	-7.938			
450	318	26.489	-8.663	6.722	48.521	0.974
	308	25.212	-8.264			
	298	23.081	-7.777			
	288	20.356	-7.215			

Outcomes show that the distribution coefficients decrease by increasing the initial concentration of solute. The raise of temperature leads to the increase of k_d, implying that high temperatures are favorable for copper biosorption. The same phenomenon was observed in other adsorption systems [15,16]. The negative values of ΔG° denote that the adsorption process is spontaneous and the degree of spontaneity of the reaction increases with increasing temperature. Enthalpy changes ΔH° were positive, indicating the endothermic nature of the adsorption process. This suggests that the transfer of copper ions from the aqueous phase to the solid phase requires energy. As the initial concentration of adsorbate increased the endothermic behavior of the sorption process decreased, implying that the adsorption reaction requires less energy. The positive values of entropy reveal an increased randomness between solid/solution interfaces during the adsorption of copper on ArNS, which is probably the effect of the release of water molecules from the hydration shell of copper ions [29].

Conclusions: -

The present paper reveals that Argan nut shell seems to be an effective and environment-friendly biosorbent for removing the copper ions from aqueous solutions. The modeling results obtained by applying pseudo-first and pseudo-second order kinetic models, in their classical and fractal forms, indicate that the fractal-like pseudo-first order is the best-fitting model for the kinetic data of ArNS−Cu. The fractal exponent increases by increasing the initial concentration of copper and it decreases by the raise of temperature. The increase of the initial concentration of adsorbate or the temperature results in an increase in the kinetic constants of the f-PFO model. The adsorption half-time decreases by increasing the initial concentration of solute or the temperature. The distribution coefficient is affected by the variation of the initial concentration of adsorbate and the temperature. Outcomes show that the increase of the temperature favors the copper biosorption, while the rise of the initial solute concentration leads to the decrease in kd. The negative $\Delta G°$ values but positive $\Delta H°$ and $\Delta S°$ values indicate that the adsorption of copper ions is a spontaneous process for which the driving force is entropy.

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