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Comparision of Langmuir and Freundlich Equilibriums in Cr, Cu and Ni Adsorption by *Sargassum*

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ABSTRACT

Heavy metals are present in different types of industrial effluents, being responsible for environmental pollution. Biosorption is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. In this work application of Langmuir and Freundlich sorption models for chromium, copper and nickel biosorption process by *Sargassum* seaweed biomass was studied in batch system. The work considered the effects of some important parameters such as retention time and initial concentration on remained concentration of heavy metals. Dried *Sargassum* was contacted with metal solution on different retention times (10, 20, 30, 45 and 60 min) and variation of initial concentration (10, 25, 50, 75 and100mg/l) at constant pH and temperature. The obtained charts were linear for Langmuir and Freundlich equilibriums and their slopes and y-intercepts were calculated (Constants a, b, n, k). Results showed that the constants were in a same range; therefore Langmuir and Freundlich sorption models were in good agreement with experimental results.

Keywords*:* Sargassum, *Heavy metals, Langmuir, Freundlich*

INTRODUCTION

Mining activities, agricultural run off, industrial and domestic effluents are mainly responsible for the increase of the metals released into the environment. Metals that are released into the environment tend to persist indefinitely, accumulating in living tissues throughout the food chain and are posing a serious threat to the environment and public health (Aksu and Kutsal, 1991).
There are numerous methods currently employed to remove and recover the metals from our environment. These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electroprecipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, etc. These methods differ in their effectiveness and cost. They also often tend to treat the metal totally as waste without the possibility of recycling. Experiments showed that most of conventional methods produce some complexes with other compounds and interfere with other treatment processes or environment. On the other hand they are costly for low concentration wastes; but biological methods are economical for these situations. The live or dead algae are used to treat hazardous wastes

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for elimination of organics and minerals. Algae are able to eliminate different forms of heavy metals by chelating, making complexes, catalyzing or adsorption.

Application of live algae, although more efficient, is difficult for industries, because some special precautions on con- ditions should be met, such as temperature, light, pH, etc (Leusch et al., 1995; Volesky, 2000). Biological absorptions which are only possible by live organisms are done slowly and include surface adsorptions and inter cellular absorption. Separation mechanism of Cu, Cr, and Ni by dried biomass of *Sargassum* is surface adsorption and independent of metabolisms. Absorption accomplishes by exchanges of metal cations with active groups of cellular walls. Carboxyl algenic acids do most absorption and produce dentate compounds. The other mechanism of absorption is by sulfate groups of cellular walls.

The Langmuir model predicts the formation of an adsorbed solute monolayer, with no side interactions between the adsorbed ions. It also assumes that the interactions take place by adsorption of one ion per binding site and that the sorbent surface is homogeneous and contains only one type of binding site. The Freundlich model does not predict surface saturation. It considers the existence of a multilayered structure (Fourest and Volesky, 1996; Wallace et al., 2003).

MATERIALS AND METHODS

The biomasses used in the present study were the brown seaweed *Sargassum* collected in Queshm island of Persian Gulf and dried under the sun to be used in the experiments. The algae were extensively washed with diluted acid and distilled water to remove particulate material and salts from the algae; further, they were oven-dried at 60ºC to the fixed weight. Parts of this biomass were examined for metals in question as control for experiment calculation. All glass and other instruments were washed with detergent and distilled water to be free from any precontaminations.

Experimental solutions were prepared in laboratory with:

%99.5 $Cu(NO_3)_2 . 3H_2O$

%98 $Cr(NO_3)_3 . 9H_2O$

%97 $Ni(NO_3)_2 . 6H_2O$

Solution of 1000 mg/l of each metal was prepared as stock solution and diluted to 10, 25, 50, 75 and 100 mg/l for the experiment.

Atomic absorption spectrometer (Varian–200) was used for analysis of artificial waste before and after exposure to algae.

The effect of different retention times (10, 20, 30, 45 and 60 min) with variation of initial concentration (10, 25, 50, 75 and 100mg/l) at constant pH and temperature on removal of heavy metals by dried mass of *Sargassum* was considered in batch system. Experiments to determine the retention time effect for sorption were performed in Erlenmeyer flasks, using 200 ml of metal solution (10, 25, 50, 75 and 100 mg/l) and approximately 5 grams of dried biomass (each gram of *Sargassum* adsorbs 5 milli mole metals) (Barkhordar, 2003). The flasks were maintained at 22ºC and pH~5.5 for Cu, Ni and pH~3.5 for Cr (pH and temperature were not effective on heavy metals adsorption by *Sargassum*) (Barkhordar, 2003) under constant agitation in a rotator shaker. Samples (1 ml) were removed at different time intervals (10, 20, 30, 45 and 60 min), membrane filtered (0.45 µm pore size) and analyzed for heavy metals by atomic absorption spectroscopy.

The adsorption isotherms were found to follow the typical Langmuir and Freundlich sorption models.

Metal biosorption coefficient (q) and construction of sorption isotherms was calculated from the initial concentration (C_i) and the final or equilibrium con- centration (C_e) in every flask.

For Langmuir isotherm, 1/x/m and $1/C_e$ were drawn on vertical and horizontal axis respectively. If the obtained chart becomes linear, its slope would be 1/ab and its y-intercept is 1/b.

For Freundlich isotherm, logx/m on vertical axis and logC_e on horizontal axis were drawn. If the obtained chart becomes linear its slope is 1/n and its y-intercept is logK.
Langmuir and Freundlich sorption isotherms and their regression (least squares method) were drawn with experimental data (Valko and Vagda, 1987).

RESULTS

Langmuir and Freundlich sorption isotherms are presented in Figures 1-6. Experimental results showed that the kinetics of heavy metals biosorption by inactive biomass of the marine alga *Sargassum* reaches to total biosorption capacity in ten minutes.
The obtained coefficients and constants, significance, correlation and R^2 from linear regression of Langmuir model are presented in Tables 1, 3 and 5. The obtained coefficients for 1/n and K constants, significance, correlation and R^2 from linear regression of Freundlich model are presented in Tables 2, 4 and 6. Their regression (least squares method) was drawn with experimental data. All charts were linear (their regression lines were acceptable) and obtained constants were in a same range. Therefore results were in good agreement with the experimental data.

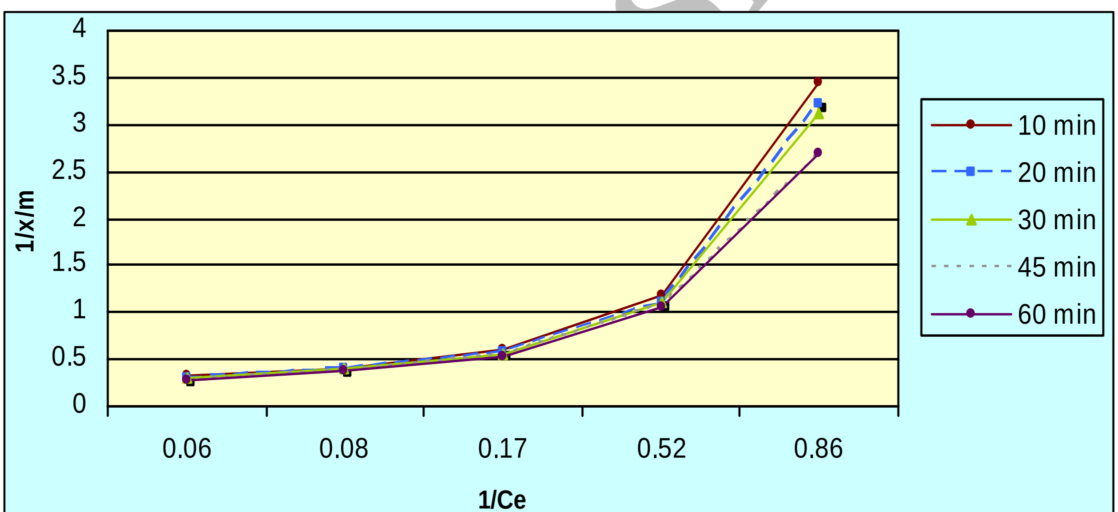

Fig. 1: Drawing Langmuir sorption models for Cu with experimental data

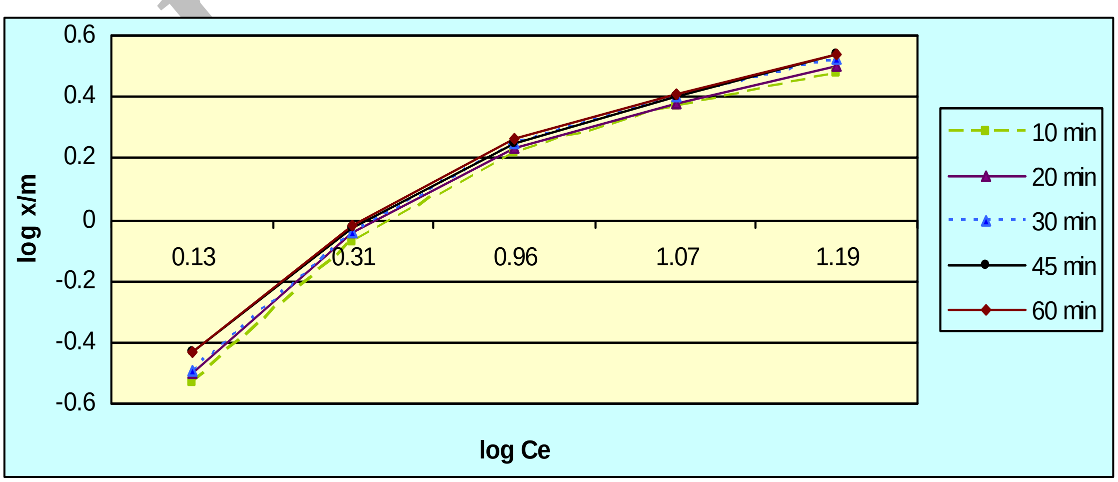

Fig. 2: Freundlich sorption models for Cu with experimental data

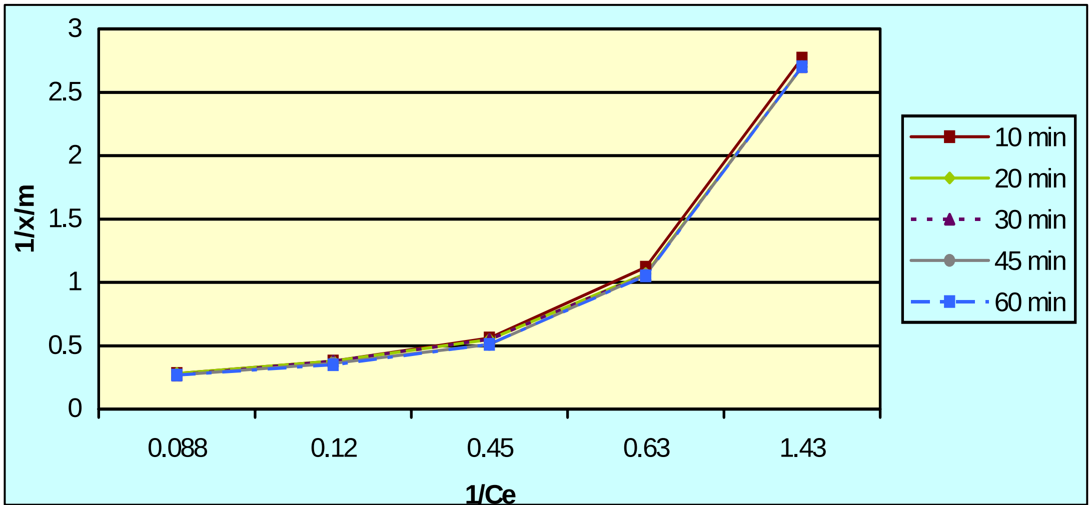

Fig. 3: Langmuir sorption models for Cr with experimental data

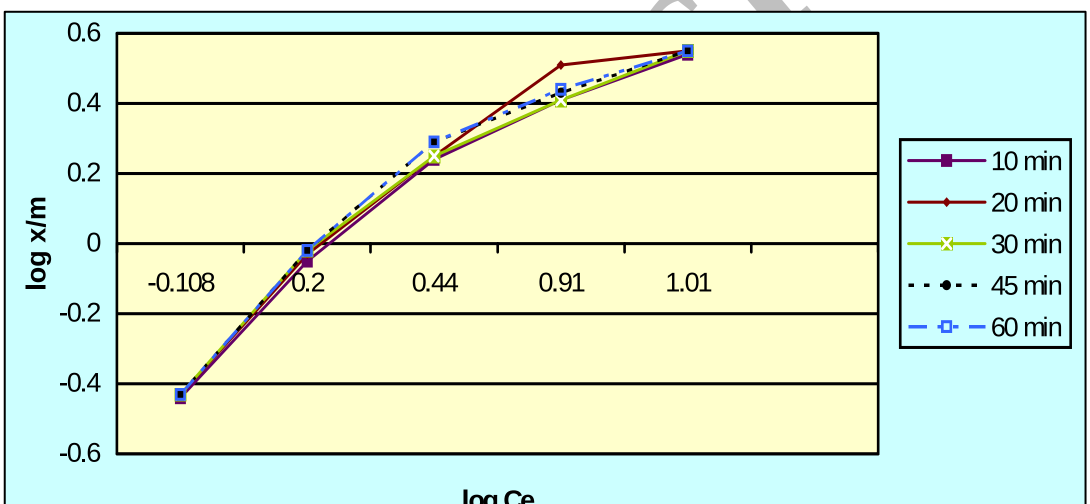

Fig. 4: Freundlich sorption models for Cr with experimental data

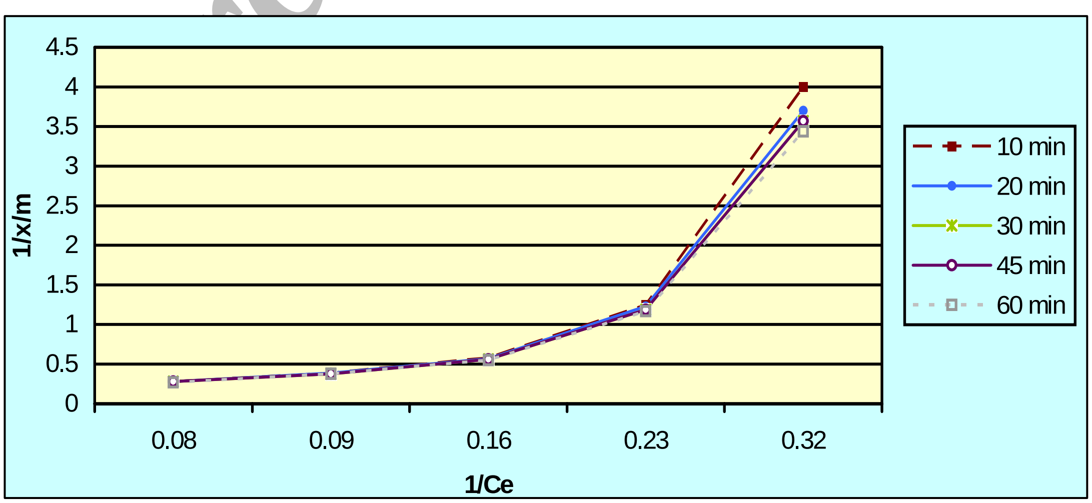

Fig. 5: Langmuir sorption models for Ni with experimental data

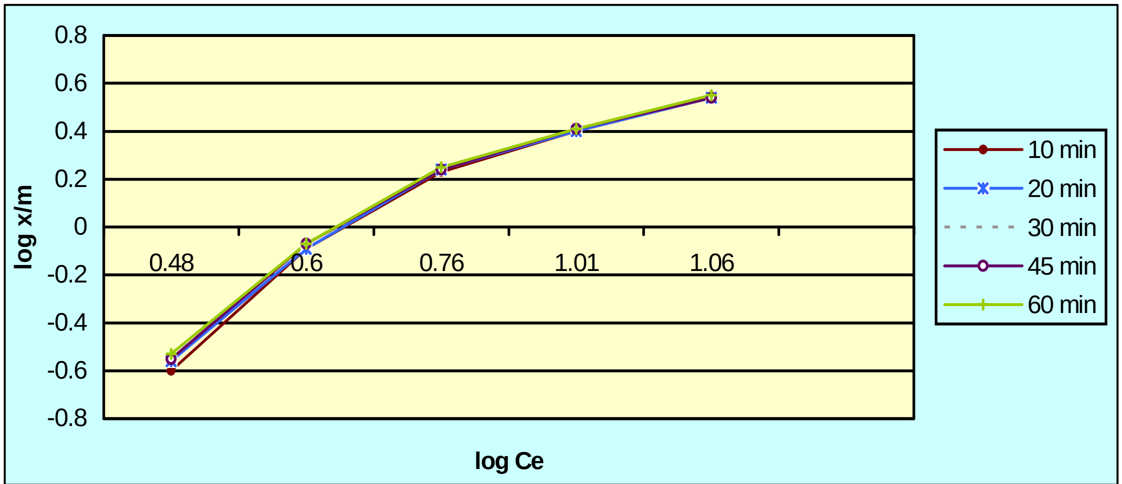

Fig. 6: Freundlich sorption models for Ni with experimental data

Table 1: Slope and y-intercept obtained from Langmuir sorption model for Cu

Confidence interval %90 (constant e) for 1/ab		Confidence interval %90 (constant e) for1/b		a	b	1/ab	1/b	R^2	Sig.
Down interval	Up interval	Down interval	Up interval						
4.768	12.900	-1.089	0.575	-0.029	-3.891	8.834	-0.257	0.863	0.022
1.213	9.597	-1.221	0.109	-0.012	-15.372	5.405	-0.065	0.689	0.050
1.863	7.567	-1.077	0.795	-0.029	-7.092	4.715	-0.141	0.785	0.046
1.569	2.153	-0.065	0.323	0.069	7.751	1.861	0.129	0.982	0.001
1.040	1.800	-0.180	0.472	0.102	6.849	1.420	0.146	0.949	0.005

Table 2: Slope and y-intercept obtained from Freundlich sorption model for Cu

Confidence interval %90 (constant e) for1/n		Confidence interval %90 (constant e) for K		n	1/n	K	R^2	Sig.
Down interval	Up interval	Down interval	Up interval					
0.636	1.372	-1.154	-7.668	0.994	1.004	-0.802	0.909	0.012
0.443	1.279	-0.943	-0.203	1.161	0.861	-0.573	0.850	0.026
0.509	1.305	-0.839	-0.199	1.102	0.907	-0.519	0.874	0.020
0.560	0.884	-0.387	-0.147	1.385	0.722	-0.267	0.963	0.003
0.468	0.840	-0.309	-0.041	1.529	0.654	-0.175	0.943	0.006

Table 3: Slope and y-intercept obtained from Langmuir sorption model for Cr

Confidence interval %90 (constant e) for1/ab		Confidence interval %90 (constant e) for1/b		a	b	1/ab	1/b	R^2	Sig.
Down interval	Up interval	Down interval	Up interval						
1.750	2.194	0.089	0.361	0.114	4.444	1.972	0.225	0.991	0.000
1.578	2.104	-0.041	0.311	0.073	7.407	1.840	0.135	0.985	0.001
1.485	2.109	-0.105	0.327	0.061	9.009	1.797	0.111	0.978	0.001
0.686	2.478	-0.779	0.696	-0.026	-23.866	1.582	-0.041	0.806	0.039
0.714	2.250	-0.786	0.609	-0.059	-11.353	1.482	-0.088	0.832	0.031

Table 4: Slope and y-intercept obtained from Freundlich sorption model for Cr

Confidence interval %90 (constant e) for1/n		Confidence interval %90 (constant e) for K		n	1/n	K	R^2	Sig.
Down interval	Up interval	Down interval	Up interval					
0.722	0.902	-0.433	-0.297	1.231	0.812	-0.365	0.991	0.000
0.587	0.907	-0.387	-0.155	1.338	0.747	-0.271	0.966	0.003
0.584	0.932	-0.373	-0.129	1.319	0.758	-0.251	0.962	0.003
0.198	1.118	-0.361	0.186	1.519	0.658	-0.087	0.732	0.054
0.234	1.118	-0.305	0.190	1.479	0.676	-0.057	0.758	0.050

Table 5: Slope and y-intercept obtained from Langmuir sorption model for Ni

Confidence interval %90 (constant e) for1/ab		Confidence interval %90 (constant e) for1/b		a	b	1/ab	1/b	R^2	Sig.
Down interval	Up interval	Down interval	Up interval						
7.717	25.805	-2.782	0.286	-0.074	-0.801	16.761	-1.248	0.821	0.034
7.881	19.613	-2.148	0.052	-0.076	-0.954	13.747	-1.048	0.880	0.018
5.379	17.875	-2.204	0.364	-0.079	-1.086	11.627	-0.920	0.822	0.034
5.339	16.835	-2.181	0.315	-0.084	-1.071	11.087	-0.933	0.832	0.031
4.629	16.533	-2.382	0.346	-0.096	-0.982	10.581	-1.018	0.808	0.038

Table 6: Slope and y-intercept obtained from Freundlich sorption model for Ni

Confidence interval %90 (constant e) for1/n		Confidence interval %90 (constant e) for k		n	1/n	K	R^2	Sig.
Down interval	Up interval	Down interval	Up interval					
1.103	2.503	-2.039	-0.819	0.554	1.803	-1.429	0.898	0.014
1.177	2.237	-1.744	-0.844	0.585	1.707	-1.294	0.932	0.008
0.988	2.176	-1.604	-0.636	0.632	1.582	-1.120	0.904	0.013
0.999	2.167	-1.563	-0.627	0.631	1.583	-1.095	0.907	0.012
0.941	2.337	-1.593	-0.537	0.610	1.639	-1.065	0.880	0.018

DISCUSSION

The kinetics of heavy metals biosorption by inactive biomass of the marine alga *Sargassum* were fast, reaching 60% of the total biosorption capacity in ten minutes.
All charts were linear (their regression line was acceptable) and all of the data obtained for isotherm constants in different experiments were in a same range and on echelon type after equilibrium time. The amount of constants was between up and down range of confidence interval of %90; hence Langmuir and Freundlich sorption models were in good agreement with experimental results.
The results showed that both models, Langmuir and Freundlich, fit reasonably well with the experimental data. Differences between the experimental and predicted values were 3.0% and 3.5%, respectively. This may be acceptable if the complex structure of the algae surface is considered,where many chemical groups can contribute on the biosorption process. None of the tested models had taken into account this phenomenon.
These isotherms have been frequently used to fit experimental data (Holan et al.1993; Holan and Volesky, 1994; Leusch et al. 1995; Costa et al. 1996) in studies with different metals and biomass. In general, the results were in good agreement with the experimental data.

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