

The Potential of *Sargassum oligocystum* Harvested From Persian Gulf for the Adsorption of Copper Ions From Aqueous Solutions

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Abstract

This study revealed the potential of a brown alga, *Sargassum oligocystum*, harvested from Persian Gulf for the Cu²⁺ adsorption from aqueous solutions. The adsorption kinetic and isotherm and the characteristics of the biomass prepared from *S. oligocystum* (BSO) were investigated. The BSO was a mesoporous adsorbent with Brunauer, Emmett, and Teller (BET) surface area, a total pore volume, and an average pore diameter of 0.487 m²/g, 1.423 cm³/g and 12.5 nm, respectively. Fourier transform infrared spectroscopy (FTIR) analysis showed that there were many active functional groups such as alcohol and phenol groups, carbonyl, ethers, and esters on the BSO. Batch tests demonstrated that the Langmuir isotherm model best represented the equilibrium data with maximum copper ions adsorption capacity of 8.23 mg/g. Pseudo-second-order kinetic model was found to satisfactorily describe the adsorption process. BSO is an easy-prepared adsorbent and could be an option for the treatment of Cu²⁺-laden wastewaters.

Keywords: Mesoporous Adsorbent, Copper Ions, Isotherm, Kinetic, *Sargassum oligocystum*

1. Introduction

The removal of heavy metals including copper ions is considered an important issue from the environmental and economical point of view. Several techniques such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and biological processes have been successfully applied for detoxifying heavy metals from industrial wastewaters (1-3). However, the feasibility of these techniques economically and technically may limit their implementation (4). Adsorption is a technique that uses low or no-cost biomass to sequester heavy metals and is especially useful for the removal of pollutants from industrial wastewaters (5, 6). The adsorption process offers several benefits such as low operating cost, minimization of the volume of sludge to be disposed of, high efficiency in removing very dilute effluents, and no nutrient requirements. These advantages have led to the primary incentives for developing full-scale adsorption processes to clean up heavy metal contamination.

In this context, living and non-living plants, animals and microorganism cells are able to separate heavy metal ions from aqueous solutions. The uptake of heavy metal ions by microorganisms may offer an option for their re-

moval from wastewaters. For such application, yeast (7), bacteria (8), fungi (9-11), and algae (5, 12-14) were assessed as adsorbents for the removal of heavy metals. The aforementioned articles demonstrated that algal adsorbents might be effective, particularly when they exist in dead cells forms. Algae biomass is easily available in abundant quantities. Algae, in particular marine brown ones such as *Sargassum oligocystum*, can also be easily grown in sea water and cultivated in substantial amounts using simple techniques and inexpensive growth media. Therefore, algae biomass could be an alternative as an economical means for the removal/recovery of metal ions from aqueous solutions.

As reported by Luna et al. (15), the biomass of brown algae of the *Sargassum* genus is a superior adsorbent to other organic and inorganic adsorbents. Therefore, the aim of this paper was to assess the *Sargassum oligocystum* harvested from Persian Gulf for eliminating copper ions as a model of heavy metals. According to world health organization (WHO) and environmental protection agency (EPA) guidelines, the maximum allowed concentration of Cu²⁺ ion in drinking water is 1.3 mg/L and 2.0 mg/L, re-

spectively (16). The kinetic and equilibrium study as well the characteristics of biomass of *S. oligocystum* (BSO) as an adsorbent was performed.

2. Materials and Methods

2.1. Preparation of the Adsorbent

The brown algae (*S. oligocystum*) were harvested from the coast of Persian Gulf, Bushehr city, Iran. The adsorbent was prepared according to the literature (17, 18). Initially, the algae were washed with tap water. The BSO was dried in an oven at 140°C for four hours and then the dried mass was ground and sieved to obtain uniform size fractions. The 0.30 - 0.45 mm particle fraction was used as adsorbent in the tests.

2.2. Chemical

All the chemicals and reagents used in this study were of analytical grades and were purchased from Sigma Aldrich Co (U.S). The stock solution of Cu^{2+} (1.0 g/L) was provided using CuCl_2 and was diluted as desired to make working solutions. The solutions pH was regulated with 1 M HCl and NaOH.

2.3. Experiments Design

Adsorption experiments were performed in a rotary shaker at 150 rpm and 20°C using 250 mL shaking flasks containing 100 mL of different concentrations of copper chloride. The initial pH value of the solution was adjusted with HCl or NaOH using pH meter; 0.10 g of the BSO was added to each flask. After shaking the flasks for a predetermined time, the reaction mixture was filtered through a filter paper and the filtrate was analyzed. The concentration of the copper adsorbed by the BSO was calculated according to the initial and equilibrium concentration of copper, the volume of solution, and the biomass weight. All the tests were performed in triplicate and the averages of values were stated herein. The SPSS software (version 19) was applied to analyze the data. Equations 1 were applied to determine the copper removal efficiency (CRE) and the adsorption capacity (mg/g) (19).

$$(1) \quad \text{CRE (\%)} = \left(\frac{C_i - C_t}{C_i} \right) \times 100$$

$$(2) \quad q_e \left(\frac{\text{mg copper}}{\text{g LW}} \right) = (C_i - C_e) \times \frac{V}{M}$$

2.4. Kinetic Experiments

Kinetic experiments were conducted using flasks containing 100 mL of different concentrations of 20, 40, and 60 mg/L copper. In each test, 100 mL of Cu^{2+} solution with the desired concentration was added to each flask;

the pH was adjusted to 7 and the adsorbent content was adjusted to 1 g/L. After the adjustments, the resultant suspension was stirred at 150 rpm for 3 - 80 minutes at 20°C. Upon completion, the suspension was filtered and the filtrate was analyzed for residual Cu^{2+} . The results were analyzed for fitness with pseudo-first and -second-order models to determine the order and constant rate of Cu^{2+} adsorption onto BSO. The pseudo-first and -second-order models linear equations were generally as expressed in Equations 3 (20, 21):

$$(3) \quad \ln(q_{e,\text{meas}} - q_t) = \ln(q_{e,\text{calc}}) - k_1 t$$

$$(4) \quad \frac{t}{q_t} = \frac{l}{k_2 q_{e,\text{calc}}^2} + \frac{l}{q_{e,\text{calc}}} t$$

All the parameters were described in the "nomenclature" section.

2.5. Isotherms Experiments

To evaluate the isotherms of Cu^{2+} adsorption onto BSO, a series of experiments were conducted. To this end, 100 mL of a solution containing 5, 10, 20, 40, 60, and 100 mg/L of Cu^{2+} with a pH of 7 was poured into six vessels. Thereafter, 0.1 g of BSO was added to each flask. The flasks were subsequently stirred at a controlled temperature (20°C) for eight hours at 150 rpm to achieve equilibrium. Upon completion, the suspensions were filtered and the filtrates were analyzed for residual Cu^{2+} . Several isotherm models were evaluated for fitness with experimental data. The isotherm equations are presented in Table 1 and the constants of the isotherms are described in the "nomenclature" section (22).

2.6. Analysis

To identify the functional groups present on the surface of the BSO, Fourier transform infrared (FTIR) spectra were collected between 450 and 4000 cm^{-1} using an ABB Bomem FTLA 2000-102 instrument. The specific surface area and the pore size of BSO were measured using Brunauer, Emmett and Teller (BET) method with a micrometrics particle size analyzer (model ASAP 2000). The solution pH was determined by a pH meter (METTLER TOLEDO FE20). The concentration of copper ions in the solution was measured by atomic adsorption spectrophotometer (Hitachi 180 - 80).

3. Results and Discussion

3.1. Characteristics of Adsorbent

The BET surface area, the total pore volume, and the average pore diameter of BSO samples were obtained 0.487 m^2/g , 1.423 cm^3/g , and 12.5 nm, respectively. The results showed that BSO was a mesopore adsorbent. The specific surface area of BSO was 0.487 m^2/g , which was sup-

ported by the data stated in other researches (17, 23-25). The strong interaction between adsorbate ions and pore walls further controls the filling of mesopores during the adsorption process.

FTIR analysis is primarily used to identify the functional groups present in the adsorbent. The data related to FTIR spectra before and after Cu^{2+} adsorption are presented in Figure 1 and Table 2. The corresponding assignments identified for the BSO are listed in Table 2 according to the previous literatures (24, 26). From Table 2, it is revealed that the nitrogen and sulfur groups were absent in the BSO structure, whereas we noted the presence of different oxygen groups, mainly alcohol and phenol groups, carbonyl, ethers and esters. Hence, the good adsorption properties of the BSO towards Cu^{2+} ions could be attributed to the presence of these functional groups. As shown in Figure 1, the peak shifts in the spectra after Cu^{2+} adsorption indicated the active role of the functional groups of BSO for copper removal. Similar results for the adsorption of heavy metals on different species of algae have been previously reported by others (5, 6, 27).

3.2. Kinetic Behavior

The kinetic behavior of the adsorption process is a main factor in the adsorption system design when determining the adsorbent uptake rate (20). Therefore, to assess the mechanism of copper adsorption, the experimental data was fitted with the pseudo-first- and -second-order kinetics model at different test conditions.

Beside the R^2 parameter in kinetic studies, the validity of kinetic models for the adsorption data was further evaluated by calculating the average relative error (ARE) (28), which can be described as (Equation 5):

$$(5) \quad \text{ARE} = \sum_{i=1}^N \left[\frac{q_{e,\text{meas}} - q_{e,\text{calc}}}{q_{e,\text{meas}}} \right]_i$$

The information from the kinetic model derived from the corresponding plots (Figure 2) is presented in Table 3. Table 3 demonstrates the kinetic results obtained from the models. Further evaluation of the experimental data in Table 3 indicated that first, the ARE values for all three tested concentrations in the pseudo-second-order model were lower than that of the pseudo-first-order model, which confirmed the pseudo-second-order kinetic model for providing the appropriate fitness for the adsorption of copper onto BSO for the three studied initial copper concentrations. The results indicated that chemical adsorption likely controlled the adsorption of copper onto the BSO, which may imply valence forces via sharing or exchanging of electrons between copper and BSO (29). Second, as shown in Table 3, the model-calculated adsorption capacity ($q_{e,\text{calc}}$) from the pseudo-second-order model was very close to the experimental adsorption capacity ($q_{e,\text{meas}}$) under selected conditions, which affirmed the high correlation of experimental data to the pseudo-second-order model. In addition, adsorption capacity

increased, with an increase of the initial concentration, revealing that resistance to copper adsorption from the solution bulk onto BSO reduced due to the mass transfer driving force. Third, Table 3 demonstrates that the values of k_2 in the pseudo-second-order adsorption constant were 0.044, 0.007, and 0.003 for initial copper concentrations of 20, 40, and 60 mg/L, respectively. As shown, k^2 values decreased with the increase of copper. This trend indicated that the mass transfer driving force probably increased and the rate improved with an increase in the initial concentration gradient (30, 31). Other researches (32-34) have also stated the better fit of the pseudo-second-order model for data on copper ions adsorption, although they belong to adsorbents other than BSO.

3.3. Isotherm Modeling

To interpret the adsorption behavior of copper onto the BSO and its adsorption capacity, the equilibrium data attained were fitted by three isotherms (Langmuir, Freundlich, and Dubinin-Radushkevich (D-R)). The results of isotherm modelling of copper adsorption onto the BSO are given in Table 4. As shown in Table 4, the adsorption of copper onto BSO fitted well the Langmuir model with the highest values of R_L , confirming that the Langmuir isotherm better represented the adsorption of copper onto BSO. This data suggested that adsorption of copper occurred on a monolayer, as assumed in the formulation of the Langmuir model onto the BSO surface. This experimental data is in consistent with most other available data (35-38). A dimensionless separation factor or equilibrium constant R_L (20), was used to further evaluate the favorable Langmuir isotherm model (Equation 6).

$$(6) \quad R_L = \frac{1}{(1 + K_L C_0)}$$

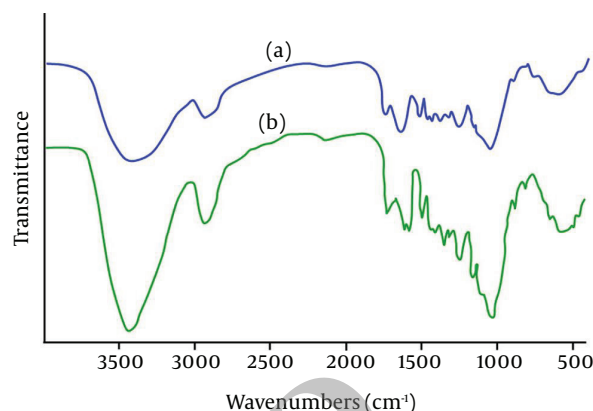
The value of R_L represents the adsorption situations to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Based on the Langmuir constant, the value of R_L for copper adsorption with BSO falls between 0 and 1, which affirmed that copper adsorption was favorable under the selected conditions of this study. In addition, it is known that $1/n$ in the Freundlich model is adsorption intensity and the values of $1/n$ indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), or unfavorable ($1/n > 1$) (22). As shown in Table 4, the $1/n$ of the Freundlich isotherm obtained was 0.448, which revealed that copper was favorably adsorbed onto BSO. Isotherm experimental data were further interpreted by the D-R isotherm to distinguish between physical and chemical adsorption. Analysis of data with the D-R isotherm indicated that the energy of the copper adsorption process onto BSO was 8 to 15 kJ/mol (Equation 7). Values of E indicated that the mean adsorption-free energy was one mole of adsorbent when is transferred to the surface of the adsorbent from the aqueous phase in the solution, which described that the adsorption mechanism

was ion-exchange or physical adsorption.

$$(7) \quad E = \left(\frac{1}{2K_{DR}}\right)^{\frac{1}{2}}$$

As presented in Table 4, values of E were in the typical range of bonding energy for chemisorption (8 - 16 kJ/mol) (22), which demonstrated that in the adsorption of copper onto BSO, ion-exchange and chemisorption played a key role. This data reconfirmed the result obtained from the kinetic study. The maximum adsorption capacity (q_{max}) of copper onto BSO was 8.23 mg/g (Table 4), which was higher than other adsorbents used for copper adsorption (29, 30, 38). Therefore, it can be suggested that copper was favorably adsorbed onto BSO and that BSO was an appropriate adsorbent due to its high adsorption capacity, abundant availability at no-cost, and economic adsorbency for the uptake of copper from industrial wastewater.

Figure 1. Fourier Transform Infrared Spectra of *Sargassum oligocystum*



A, dry unloaded biomass; B, Cu²⁺-loaded biomass.

Table 1. Linearized Expressions of Adsorption Isotherms^a

| Isotherm | Linearized Form | Plot | Parameters |
|------------|---|----------------------------|---|
| Langmuir | $\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ | $\frac{C_e}{q_e}$ vs C_e | $q_{max} = \frac{1}{slope}$, $K_L = \frac{slope}{intercept}$ |
| Freundlich | $lnq_e = lnk_f + n^{-1}lnC_e$ | lnq_e vs lnC_e | $K_f = exp(intercept)$, $n = \frac{1}{slope}$ |
| D-R | $lnq_e = lnq_m - K_{DR} \epsilon^2$ | lnq_e vs ϵ^2 | $q_m = exp(intercept)$, $K_{DR} = -slope$ |

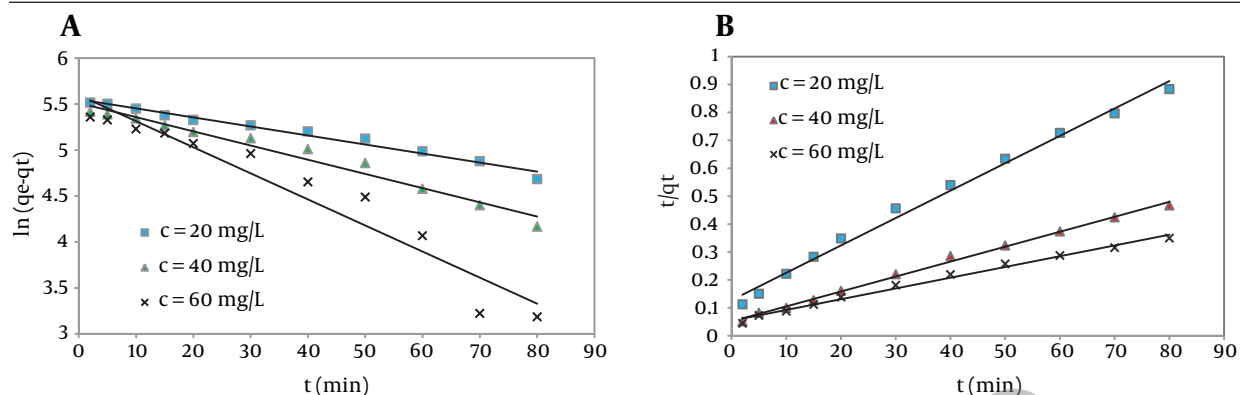
^aAbbreviations are listed in Table 5.

Table 2. Fourier Transform Infrared Spectra Absorption Bands and Assignments of the Biomass of *Sargassum oligocystum*^a

| Band, cm ⁻¹ | Vibration | Assignment |
|------------------------|-------------------|--|
| 3400 - 3405 | st O-H | Phenolic OH and aliphatic OH |
| 2960 - 2925 | st C-H | CH ₃ and CH ₂ groups |
| 1738 | st C=O | Carbonyl groups |
| 1651 | C=O asymmetric st | Carboxylic groups |
| 1510 | st C=C | Aromatic rings |
| 1462 | C-H deformation | -CH ₃ and -CH ₂ - |
| 1425 | st C-O | Carboxylic groups |
| 1377 | C-H deformation | -CH ₃ and -CH ₂ - |
| 1323 | st C-O | Carboxylate groups |
| 1246 | C=O deformation | Carboxylic acids |
| 1048 | st C-O-C and O-H | Polysaccharides |

^aAbbreviation: st, stretching.

Figure 2. Kinetic Models



A, pseudo-first order kinetic model; B, pseudo-second order kinetic model.

Table 3. Results of Kinetic Study of Copper Adsorption Onto the Biomass of *Sargassum oligocystum*^a

| Concentration, mg/L | q_e' , meas, mg/g | q_e' , calc, (mg/g) | k | ARE | R ² | Equation of Fitted Model |
|----------------------------------|---------------------|-----------------------|-------|-------|----------------|---|
| Pseudo-First-Order Model | | | | | | |
| 20 | 19 | 3.3 | 0.072 | 27.5 | 0.969 | $\ln(q_e'_{\text{meas}} - qt) = 1.939 - 0.072t$ |
| 40 | 44 | 35 | 0.056 | 34.55 | 0.868 | $\ln(q_e'_{\text{meas}} - qt) = 3.555 - 0.056t$ |
| 60 | 66.6 | 51 | 0.064 | 42.8 | 0.898 | $\ln(q_e'_{\text{meas}} - qt) = 3.932 - 0.064t$ |
| Pseudo-second-order model | | | | | | |
| 20 | 19 | 19.5 | 0.044 | 4.77 | 0.989 | $t/q_t = 0.009275 + 0.020t$ |
| 40 | 44 | 46.3 | 0.007 | 7.55 | 0.998 | $t/q_t = 0.015405 + 0.010t$ |
| 60 | 66.6 | 71.3 | 0.003 | 7.67 | 0.997 | $t/q_t = 0.019424 + 0.008t$ |

^aAbbreviations are listed in Table 5.

Table 4. Langmuir, Freundlich, and D-R Adsorption Isotherm Parameters^a

| Isotherm Model/ Parameters | Value |
|----------------------------|-------|
| Langmuir | |
| K_L | 0.09 |
| q_{max} | 8.23 |
| R_L | 0.31 |
| R^2 | 0.989 |
| Freundlich | |
| K_F | 1.19 |
| $1/n$ | 0.448 |
| R^2 | 0.995 |
| D-R | |
| K_{DR} | 0.004 |
| E | 11 |
| R^2 | 0.886 |

^aAbbreviations are listed in Table 5.

Table 5. Nomenclature

| Abbreviation | Description |
|--------------|--|
| K_{DR} | Dubinin-Radushkevich isotherm constant (mol^2/kJ^2) |
| C_e | Equilibrium concentration, mg/L |
| C_i | Copper initial concentration, mg/L |
| C_t | Copper final concentration, mg/L |
| C_e | Copper equilibrium concentration, mg/L |
| E | Free energy, kJ/mol |
| k_1 | Pseudo-first order rate constant, 1/min |
| k_2 | Pseudo-second order rate constant, mg/g.min |
| K_L | Langmuir isotherm constant, L/mg |
| M | Mass of BSO, g |
| q_e | Amount of copper adsorbed per gram of BSO at equilibrium, mgcopper/g BSO |
| $q_{e,calc}$ | Calculated q_e value, mg/g |
| $q_{e,meas}$ | Experimentally measured q_e value, mg/g |
| q_{max} | Maximum amount of copper adsorbed per gram of BSO, mgcopper/g BSO |
| q_t | Adsorption capacity at time t, mg/g |
| V | Solution volume, L |
| ϵ | Polanyi potential, J/mol |

^aAbbreviation: BSO, biomass of *S. oligocystum*.

4. Conclusions

In the present work, copper ions removal from aqueous solutions using dried alga *Sargassum oligocystum* as an adsorbent was studied in a batch mode. Investigating the adsorbent properties such as FTIR, BET surface area, the total pore volume, and the average pore diameter was one of the main purposes of this study. Equilibrium data well fitted the Langmuir isotherm model and the maximum adsorption capacity of the BSO for copper ions was 8.23 mg/g. The adsorption kinetic analysis indicated that the pseudo-second-order reaction can be used to predict the adsorption kinetics, which suggested that the process was controlled by chemisorption. Overall, it was found that the adsorbent used had an acceptable potential for copper ions removal.

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