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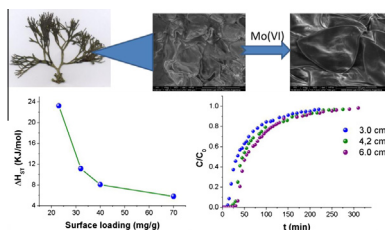
Application of green seaweed biomass for Mo^{VI} sorption from contaminated waters. Kinetic, thermodynamic and continuous sorption studies



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GRAPHICAL ABSTRACT



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ABSTRACT

Spongomorpha pacifica biomass was evaluated as a new sorbent for Mo^{VI} removal from aqueous solution. The maximum sorption capacity was found to be $1.28 \times 10^6 \pm 1 \times 10^4$ mg kg⁻¹ at 20 °C and pH 2.0. Sorption kinetics and equilibrium studies followed pseudo-first order and Langmuir adsorption isotherm models, respectively. FTIR analysis revealed that carboxyl and hydroxyl groups were mainly responsible for the sorption of Mo^{VI}. SEM images show that morphological changes occur at the biomass surface after Mo^{VI} sorption. Activation parameters and mean free energies obtained with Dubinin–Radushkevich isotherm model demonstrate that the mechanism of sorption process was chemical sorption. Thermodynamic parameters demonstrate that the sorption process was spontaneous, endothermic and the driven force was entropic. The isosteric heat of sorption decreases with surface loading, indicating that *S. pacifica* has an energetically non-homogeneous surface. Experimental breakthrough curves were simulated by Thomas and modified dose–response models. The bed depth service time (BDST) model was employed to scale-up the continuous sorption experiments. The critical bed depth, Z_0 was determined to be 1.7 cm. *S. pacifica* biomass showed to be a good sorbent for Mo^{VI} and it can be used in continuous treatment of effluent polluted with molybdate ions.

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1. Introduction

Molybdenum is an essential trace element for both plants and animals, including humans. In animals, Mo is present as a cofactor for redox enzymes such as xanthine oxidase, and it is essential for a fine performing of these enzymes [1]. In plants, this element is necessary for the fixation of atmospheric nitrogen by bacteria at the

start of protein synthesis. Nevertheless, it is harmful at high levels. It appears to be toxic when its concentration in plants is higher than $5 \mu\text{g g}^{-1}$, whereas potential toxicity for ruminants equals to $10 \mu\text{g g}^{-1}$ [2,3]. Owing to its high melting point, high strength at higher temperatures, good corrosion resistance and high thermal conductivity, molybdenum is widely used in a variety of industrial processes, such as the production of metal alloys [4]. A risk of toxic exposure of workers in these industrial fields exists and environmental contamination near the industrial plants may be possible [5]. Molybdenum occurs principally in the hexavalent oxidation state as molybdate (MoO_4^{2-}) ions, which form condensed species in acid media [6]. In strongly acidic solutions, molybdenyl cations (MoO_2^{2+}) are present [7]. The concentration of molybdenum in seawater was reported in the range of $6\text{--}20 \mu\text{g L}^{-1}$ [8] and in mineral waters in the range of $0.25\text{--}1.0 \mu\text{g L}^{-1}$ [9], far below the drinking water guidelines ($70 \mu\text{g/L}$) [10].

Molybdenum naturally occurs in various ores, especially molybdenite (MoS_2) [11,12]. Most Mo compounds have very low solubility in water [13]; however, they are easily oxidized to produce the more soluble molybdate ion (MoO_4^{2-}), which can be stable in the absence of a reducing agent.

Water soluble molybdate anions cause an environmental problem if their concentration exceeds 5 ppm [14,15]. Molybdenum in soils is primarily in the oxoanion form and is chemisorbed by iron oxides, noncrystalline aluminosilicates, organic matter, and to a lesser extent, by layer silicate clays [11]. Under reducing conditions, molybdenum is easily bioaccessible by formation of soluble thiomolybdates, e.g. MoS_4^{2-} and $\text{MoO}_2\text{S}_2^{2-}$. Phosphate as well as organic acids additions to soil may release MoO_4^{2-} from binding sites [5].

Pollution by molybdate oxoanions in groundwater represents a serious issue in the field of drinking water obtained from wells [16]. For example, Mo is present in 32.7% of surface water samples from 15 major river basins in the USA, at concentrations ranging from 2 to $1500 \mu\text{g L}^{-1}$ (mean $60 \mu\text{g L}^{-1}$). In addition, elevated Mo concentrations are reported in many mine wastes and mill tailings from North America where concentrations range from a few mg L^{-1} up to 800mg L^{-1} [17].

Therefore, the search for suitable methods for groundwater/wastewater treatment against toxic oxoanions becomes very challenging. Coprecipitation [18] and reverse osmosis [19] are methods used for these treatments but they need various and complicated equipments and reagents. Simple sorption techniques have also been reported for the removal of molybdate from aqueous solution using different sorbents like ZnCl_2 activated coir pith carbon [12], pyrite [20], carbon cloth [21], natrolite and clinoptolite-rich tuffs [22], orange peel [23], nano-ball allophone [24], $\gamma\text{-Al}_2\text{O}_3$ [25], magnetic chitosan resins [26], goethite [27], hematite [28], and modified bentonite [29].

The aim of this study is to evaluate Mo^{VI} sorption from aqueous solution in batch and column system using green seaweed biomass as sorbent. The sorbent was selected because of its natural abundance and low cost of obtaining in countries near the seas and the multiple functional groups present in its surface capable of binding Mo^{VI} species. These characteristics make this sorbent a better choice for being employed in treatment of Mo^{VI} contaminated waters. In fact, no other studies employing seaweeds in treatment of Mo^{VI} contaminated waters were reported. The sorption process has been investigated modifying different experimental parameters like pH, sorbent dosage, contact time and temperature. The competition of different anions onto Mo^{VI} sorption was also studied. The evaluation of sorption equilibrium and dynamics characteristics was done by using theoretical models in order to design and control the sorption process units. For that reason, equilibrium sorption data were applied to Langmuir, Freundlich and Dubinin–Radushkevich sorption models. Particle

diffusion simple first order and pseudo first order rate equations were used to describe sorption kinetics. Activation energy, mean free sorption energy, and thermodynamic parameters like ΔG° , ΔH° and ΔS° were also calculated. In addition, Mo^{VI} sorption was examined by FT-IR (Fourier transformed-Infrared spectroscopy), Scanning electronic microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX). Finally, green seaweed has been employed for removal of Mo^{VI} in a fixed-bed column. Some common theoretical models have been applied to fit the breakthrough curves.

2. Materials and methods

All chemicals used were of analytical reagent grade and were used without further purification. All solutions and seaweed suspensions were prepared using Milli-Q water. Mo^{VI} solutions of different concentrations were prepared by dissolving the proper amount of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma, p.a.) in water.

2.1. Biomass and pretreatment

Spongomorpha pacifica was collected at Puerto Madryn, Rio Negro, Argentina. The seaweed was carefully washed with mono distillate and Milli-Q water to remove salts, sand and microorganisms, which may interfere with the obtained results. Then, the material was dried in an oven at 40°C for 24 h, crushed in a lab mill and sieved to obtain fine particles ($0.5 < \text{size} < 1.2 \text{ mm}$). The resulting material was stored in a dry environment at room temperature. For determining the pH value at point of zero charge (pHpzc), 0.10 g of biomass was put into contact with 0.10 M NaNO_3 solution with different pH values (1.6–7.0). The suspensions were agitated for 24 h (250 rpm). The change of pH (ΔpH) was calculated as a difference between the initial pH and the equilibrium pH values. The pHpzc was identified as the initial pH with minimum ΔpH [30].

2.2. *S. pacifica* fixed in agar

A predetermined amount of seaweed biomass (size $< 0.5 \text{ mm}$) and 10.0 ml of agar solution (20.0 g L^{-1}) previously heated, were added in a beaker. The suspension was mixed and transferred to a Petri dish of known mass and dimensions. Once the seaweed/agar suspension solidified, the matrix obtained was cut into $0.5 \text{ cm} \times 0.5 \text{ cm}$ squares, which were stored in Milli-Q water in the refrigerator for later use.

2.3. Experimental design strategy. Screening design

In many cases there may be a lot of factors that seems to be important, but in reality only a few of them control the response in a significant way. The primary goal of screening designs is to identify the few factors or key variables that influence the response [31]. It is necessary to reduce the number of experiments and save time and cost. For this reason, a full 2^3 factorial design was performed. The factors considered were pH of solution, sorbent mass (m), and contact time (t). Table 1 shows the factors and their levels.

Table 1
Independent variables and their levels used for 2^3 factorial design.^a

Variables	Symbol	Range and levels	
		−1	+1
Sorbent dosage (g L^{-1})	m	2	20
Contact time (min)	t	5	120
pH	pH	1	6

^a $[\text{MoO}_4^{2-}]_0 = 3.36 \text{ mM}$; batch volume = 10.0 mL; $T = 20^\circ\text{C}$.

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