

# Kinetic Study and Isotherm Analysis of Organic Matter Adsorption by a Native Cactus from the Brazilian Backwoods

## *Estudo Cinético e Análise das Isotermas de Adsorção da Matéria Orgânica Removida por Cacto Nativo do Sertão Brasileiro*

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Under the perspective of the animal welfare, drinking water fountains are frequently reported as of poor quality, mostly due to the excess of organic matter (OM) in solution. In this study, cactus *Pilosocereus gounellei* was applied in the OM removal from samples of goat drinking water. A study of the sorption process was performed using isotherms and kinetics models of adsorption, using the sorbent *in natura* and acid treated. After mathematical treatment, isotherm of Freundlich (type C, constant partition) and pseudo-second order kinetics were the most suited. Samples treated with acid at higher concentrations removed a larger amount of OM when compared to *in natura* (up to 1.6x the own weight). Thus, based on our findings, the *P. gounellei* is an efficient alternative adsorbent material in the OM removal from natural water, intending to the good practices in livestock and animal welfare.

**Keywords:** Equilibrium isotherm; adsorptive processes; water treatment; natural organic matter; alternative sorbent materials.

## 1. Introduction

Livestock farming represents an important global economic activity, characterized by the animal creation in agricultural systems to produce labor or commodities. In addition, depending on the economic finality and/or geographical factors, two types of livestock can be applied: open systems (for instance, pastures) or confinement (corral, fowl run etc.). In both cases, practices of animal welfare are necessary and of great importance, being applied in all stages of the animal production, considering mainly the environment influence, facilities, health care, food and water supply.<sup>1-3</sup>

Several studies have reported an intrinsic relationship between animal welfare and drinking water quality. In the animals, water potability affects, for instance, the body temperature regulation, the digestion, besides metabolic processes of growth, reproduction and excretion. In addition, many studies have demonstrated that better treated animals are less stressed, resulting in higher production (e.g., eggs, wool, milk) and/or meat quality (beef cattle), occasioning in more income generation and promoting the agrarian development.<sup>4-6</sup>

An important aspect related to water quality is the level of natural organic matter (OM) in solution/suspension. In large concentration, OM causes harmful effects on animals (e.g., stress, lactation deficit, toxins synthesis etc.). Besides the losses in potability — due to the presence of color, odor and flavor — a large amount of nutrients and salts can promote a reservoir eutrophication, proliferating algae and unicellular beings, some of them potentially pathogenic.<sup>7-10</sup>

Historically, the presence of OM in water fountains was purely aesthetic: a yellowish-colored water was considered unfit for consumption.<sup>11</sup> However, nowadays, OM is described as a complex matrix of organic materials present in natural water, as a result of the interactions between the hydrosphere, soil/sediments and the biosphere. In addition, part of the OM presents in aquatic environments can be found in the form of aquatic humic substances, mostly preventient from the soil, sediment and excretion products; with potential for the proliferation of microorganisms and the transport of organic contaminants, which can seriously compromise the animal health.<sup>7,10,12</sup>

In the semi-arid, finding natural water appropriated for animal consumption is more challenging. In many regions, livestock is still practiced in archaic systems of production, also endowed with inadequate procedures that induce several animal illnesses. Particularly in the

Brazilian Backwoods, due to the irregular rainfall pattern, the supply of food and water for animal consumption is a problem. Drinking water sources are usually far and present a high level of OM. Consequently, losses on the animal weight and stress behavior are often reported, especially during dry periods, resulting in deleterious effect on the quality of the final products, decreasing the income of small ranchers.<sup>9,13,14</sup>

Several studies have reported methodologies applied for the treatment and removal of OM in natural water, for instance: precipitation, ion exchange, coagulation, flocculation, ozonation, and filtration; however, these technologies are usually limited by technical factors or economically unviable.<sup>7,15–17</sup> Thus, the using of natural-adsorbent materials is an interesting alternative to remove chemical contaminants, organic or inorganic, present in the water bodies, via adsorptive processes. Adsorption is a spontaneous process that occurs on the surface of a solid (adsorbent), when contacts the contaminant (adsorbate). Usually involves simple physical processes of just-deposition, leading to the formation of colloidal structures, being the contaminant easily operated/removed from the middle.<sup>7,15,18,19</sup> Furthermore, the search for alternative materials also comprehends the availability in the field or ranch, easy access, besides to the costs of collection, transportation and processing; in addition to presenting favorable chemical and physical characteristics of the adsorption process.<sup>7,20</sup>

In this study, xique-xique (*Pilosocereus gounellei*) was applied in the water treatment, through OM removal. *P. gounellei* is a cactus endemic from the Brazilian Backwoods (Caatinga biome), that cover ~10% of the Brazilian territory. Physiologically, *P. gounellei* is a cactus covered by thorns, which provide consistency, security, besides serving as a water reservoir. In addition, cactuses are often used as animal food support during periods of drought,<sup>21,22</sup> and there are no studies on its use in the treatment of natural waters.

Abundant and easily accessible, *P. gounellei* was applied as adsorbent material on the OM removal in natural water intended for animal consumption. Moreover, removal processes, through adsorption, involves environmental physical-chemical concepts, which can be investigated via mathematical equations, for instance, the Langmuir and Freundlich adsorption models, providing several information about interactions between adsorbent and adsorbate, in addition to characteristics of the surface covering (mono or multilayer). Thus, after data obtained, results can support essential information, important to improve the use of alternative sorbent materials, in addition to inferring on the adsorbent efficiency and their removal capacity.<sup>19,21</sup>

While Langmuir adsorption model considers the adsorption in monolayer, in addition to an absence of interaction between the adsorbed particles; Freundlich adsorption model considers the adsorption in multilayer, in

addition to a chemical and physical interaction between the adsorbed particles and the surface (mathematical equations presented in the section Materials and Methods).<sup>23,24</sup>

Regarding to the kinetics (in terms of velocity and removal time efficiency), two models are usually assessed. Pseudo-first order kinetic considers the occupation speed of the active sites proportionally to the number (quantity or concentration) of adsorbate; on other hand, pseudo-second order kinetic considers an increase in speed as a function of the square of the adsorbate concentration in solution or suspension. In general, data of kinetic/velocity can supply information about the necessary time to an optimal contaminant removal/water treatment, resulting in economy of time and money.<sup>25</sup>

Therefore, this study aimed to use the cactus *P. gounellei* — as alternative adsorbent material — in the OM removal and treatment of natural water intended for animal consumption.

## 2. Materials and Methods

### 2.1. Samples

Samples of *P. gounellei* were obtained in a cactus plantation, located at the Federal Rural University of Pernambuco (UFRPE), campus of Serra Talhada, Brazil (07°57'11"S; 38°17'41"W). Approximately 10 natural plants with 1 m in height were collected. Initially, cactus cladodes were collected and the spines removed. Thus, the material was air-dried, ground in a knife mill, and then passed through a 2 mm sieves. Approximately

Samples of goat drinking water were collected at the Espirito Santo Farm, located in the municipality of Itacuruba, Brazil (8°45'36.6"S; 3°839'37.5"W). After sampling, levels of total organic carbon (TOC) and suspended solids (SS) were determined (111.47 mg L<sup>-1</sup> and 16.67 mg L<sup>-1</sup>, respectively). Data of organic carbon were applied in the OM determination, serving as reference in the tests using real samples. TOC was determined using a Shimadzu TOC-V CPH spectrophotometer – standard mode of operation (Kyoto, Japan), and SS using a Sterilifer SX 1.0 DTMC drying oven (Tamandaré, Brazil) and an Acculab ALC210.4 analytical balance (Rocky Mount, USA).

Samplings were performed in February 2019 (34°C of temperature and 66 mm of precipitation). Sample collection, preservation, transport and storage were made in accordance with the National Guide for Sample Collection and Preservation (Brazil).<sup>26</sup>

### 2.2. Acid treatment

Acid treatment was conducted aiming to modify the vegetal tissue, leading the pores opening, able to act as an adsorption site for the OM removal, during the water treatment.

Therefore, 10 g of sample (*P. gounellei* ground and sieved) and 100 mL of HCl in the concentrations of 0.01, 0.1, 0.5, 1.0, 2.0, and 4.0 mol HCl L<sup>-1</sup> were stirred during 12 h, at room temperature (25 °C), in a water bath. Then, the suspension rested during 8 h at 60 °C to evaporate the chlorine gas (Cl<sub>2</sub>). Finally, the material was thoroughly washed with water and then air-dried.

### 2.3. Turbidity and remaining OM

Aiming to determine the turbidity, water samples were firstly homogenized on an orbital shaker at 25 rpm during 20 min and then, the suspension turbidity was immediately determined (standard mode of operation), using an Akso TU430 digital turbidimeter (São Leopoldo, Brazil).

Values of turbidity were associated with the content of OM dispersed in solution. Considering the water treatment via adsorptive processes, the content of remaining OM was determined via linear regression, using an analytical curve, built using 7 concentration points: 0.0001, 0.001, 0.01, 0.1, 0.25, 0.5, and 1.0 g OM L<sup>-1</sup>. In addition, the method sensitivity, limit of detection (LOD), limit of quantification (LOQ), and recovery were determined.<sup>27</sup>

To build the analytical curve, different solutions were prepared using a dystrophic Red-Yellow Argisol (dRYA, OM 0.21 g kg<sup>-1</sup> and TOC 0.04 g kg<sup>-1</sup>), collected in the same location where samples of goat drinking water were obtained (8°45'36.6"S; 3°839'37.5"W).

Recovery was calculated comparing the TOC measured in the water to a sample-control prepared using the dRYA. Data of TOC were determined using a Shimadzu TOC-V CPH spectrophotometer (Kyoto, Japan), equipped with a spectrophotometric detector operating in the infrared region, model SSM-5000A Shimadzu (Kyoto, Japan).

### 2.4. Water treatment

#### 2.4.1. Isotherms of adsorption

Isotherms of adsorption were constructed using 0.1 g of adsorbent (*P. gounellei* acid modified or *in natura*) added to 10 mL of aqueous suspension (goat drinking water rich in OM), in the concentrations of 0.01, 0.1, 0.25, 0.5 and 1.0 mg OM L<sup>-1</sup> (milligram of organic matter per liter of solution). The mixtures were stirred during 24 h on a shaking table and then the adsorbent was removed using a spatula. Finally, the supernatant turbidity was determined, and via linear regression, the remaining OM concentration was calculated.

Aiming to assess the adsorption process of the OM removal, two isotherms were analyzed, based on Langmuir (Equation 1)<sup>23</sup> and Freundlich (Equation 2)<sup>24</sup> adsorption models:

$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + Q_m \times C_e} \quad (1)$$

$$Q_e = K_F \times C_e^{\frac{1}{n}} \quad (2)$$

where  $Q_e$  is the amount adsorbed per gram of adsorbent,  $Q_m$  is the maximum adsorption capacity,  $K_L$  is the Langmuir constant,  $C_e$  is the equilibrium concentration,  $1/n$  is the measure of intensity, and  $K_F$  is the Freundlich constant.

Then, to determine the parameters of sorption  $C_e$ ,  $1/n$ ,  $Q_m$  and  $K_L$  or  $K_F$ , the Langmuir and Freundlich isotherms equations were linearized (Langmuir in Equation 3 and Freundlich in Equation 4). The most suitable model was selected according to the plotted equation that presented an R<sup>2</sup> closest to 1.0.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \times K_L} + \frac{1}{K_L} \times C_e \quad (3)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \times \ln C_e \quad (4)$$

#### 2.4.2. Adsorption kinetics

A study of the adsorption kinetic was conducted using 0.5 g of adsorbent (*P. gounellei* acid modified or *in natura*) added to 10 mL of aqueous suspension (goat drinking water rich in OM), constantly agitated on a shaking table and assessed at the predetermined times: 0, 0.5, 1, 6, 12, 24, and 48 h. Then, the adsorbent was removed with a spatula and the supernatant turbidity was determined. The remaining OM was calculated via linear regression.

To perform the kinetic study, two models were evaluated, based on the equations of pseudo-first order (Equation 5) and pseudo-second order reactions (Equation 6),

$$\frac{dC_{ads}}{dt} = k_1 \times (C_e - C_{ads}) \quad (5)$$

$$\frac{dC_{ads}}{dt} = k_2 \times (C_e - C_{ads})^2 \quad (6)$$

where  $C_{ads}$  is the concentration adsorbed at any time,  $C_e$  is the equilibrium concentration,  $t$  is the time,  $k_1$  is the pseudo-first order rate constant, and  $k_2$  is the pseudo-second order rate constant.

To determine the kinetic parameters  $C_e$ ,  $C_{ads}$  and  $k_1$  or  $k_2$ , the equations of the kinetic models were linearized (pseudo-first order in Equation 7 and pseudo-second order in Equation 8). The most suitable model was selected according to the plotted equation that presented an R<sup>2</sup> closest to 1.0.

$$\ln(C_{max} - C_{ads}) = \ln C_e - k_1 \times t \quad (7)$$

$$\frac{t}{C_{ads}} = \frac{1}{k_2 \times C_e^2} + \frac{1}{C_e} \quad (8)$$

Finally, the velocity of the OM removal was determined (Equation 9, if pseudo-first order; or Equation 10, if pseudo-second order), and a curve was built, indicating the quantity of OM removed per unit of time.

$$v = k_1 \times \frac{d[\text{OM}]}{dt} \quad (9)$$

$$v = k_2 \times \frac{d[\text{OM}]^2}{dt} \quad (10)$$

where  $v$  is the velocity (presented in gram of organic matter removed per hour,  $\text{g OM h}^{-1}$ ),  $k_1$  and  $k_2$  are the pseudo-first and pseudo-second order rates constant, and  $d[\text{OM}]/dt$  and  $d[\text{OM}]^2/dt$  are the OM derivation in function of the time (based on the midpoint method).

## 2.5. Statistical analysis

Procedures of acid treatment and method validation were conducted in triplicate and data tested for normality (Shapiro-Wilk test) and homoscedasticity (Bartlett test). Data Normal and homoscedastic results were presented as mean followed by the statistical significance test (ANOVA) and Duncan's new multiple range test (MRT). Statistical tests and analyzes were performed using the software IBM SPSS Statistics v.025. Licensed software.

## 2.6. Laboratory procedures

The laboratory procedures, analytical or not, were realized in accordance to the requirements, when applicable, of the ISO 17025 (General requirements for the competence of testing and calibration laboratories) and following the principles of Good Laboratory Practices (GLP), in order to guarantee data traceability and quality management.<sup>28,29</sup>

All the waste/residues generated during the development of this study was collected, labeled and conditioned immediately after produced. The treatment (recycling or incineration) was carried out according to the rules and procedures adopted at the Federal Rural University of Pernambuco (UFRPE).

## 3. Results and Discussion

### 3.1. Acid treatment

Initially, acid treatment modified the *P. gounellei* vegetal tissue, reducing mass and yield because of the acid attack on the fibers. In general, the chemical modification yield ( $\eta$ )

varied according to the chlorine acid concentration; in higher concentrations, more intense were the observed effects, resulting in a material of blacker color and, quantitatively, of a lower yield ( $\eta$ ) (m/m) (Table 1).

As the method of OM quantification was colorimetric, the addition of a dark colored sorbent (or able to darken the medium) could interfere in the turbidity, generating doubtful results.<sup>30,31</sup> Thus, after preliminary tests, only the concentrations of 0.01, 0.1, 0.25, 0.5, and 1.0 mol HCl L<sup>-1</sup> were assessed in this study, since they increased the potential of adsorption without interfering negatively on the turbidity results.

### 3.2. Analytical method validation

A method was validated aiming to aggregate reliability to the results of turbidity in natural water samples. Firstly, an analytical curve was built, ranging the concentrations from 0.0001 to 1.0 g OM L<sup>-1</sup>, and a R<sup>2</sup> of 0.9998, indicating a suitable linear correlation; in addition to small values of the uncertainties:  $S_y$  (0.44 NTU),  $S_a$  (0.99 mg OM L<sup>-1</sup>), and  $S_b$  (0.19 NTU). Among the reported uncertainty,  $S_y$  is the most important, since the turbidity values (y-axis) is strictly correlated to the calculated value of OM (x-axis) (0.44 NTU = 18.5  $\mu\text{g OM L}^{-1}$ ) (Table 2).

Regarding the method limits, results of LOD and LOQ were determined in small values of 0.12 and 0.41 mg OML<sup>-1</sup>, respectively (Table 2). These concentrations are up to 18 $\times$  smaller than the content of OM observed in natural water bodies, around 2.2 mg OM L<sup>-1</sup> in oligotrophic lakes or wells,<sup>32</sup> indicating a robust range of method operation.

Thus, considering the value of LOQ (0.41 mg OM L<sup>-1</sup>) and the highest concentration in the analytical curve (1.0 g OM L<sup>-1</sup>), the validated method presented a working range in the interval of concentrations between 0.41 mg OM L<sup>-1</sup> and 1.0 g OM L<sup>-1</sup>. In addition, values of recovery (88.6%) and sensibility (15.5) indicated a small matrix interference, as expected.

Finally, in conditions tested on this method, our findings indicated that is possible to use a turbidimeter in the OM determination in natural waters, with analytical security and reliability on the taken results. However, we consider that natural waters are a mixture of different elements, which could interfere in the turbidity results. Thus, although interferences can occur, the matrix effect was observed as the minimum as possible, without invalidating the obtained data/results. In cases of higher importance, this method could be

**Table 1.** Chemical modification yield ( $\eta$ ) (m/m) using HCl in different concentrations on the acid treatment of cactus *P. gounellei* (mean followed by Duncan's test,  $n = 3$ , on dry matter basis)

	HCl / mol L <sup>-1</sup>				
	0.01	0.1	0.25	0.5	1.0
$\eta$ (% m/m)	96.6cd	94.7cd	83.4c	77.2b	59.9a

Values in the same column followed by the same letter are not statistically different at  $p < 0.05$  from each other, according to ANOVA One-way and Duncan's test

**Table 2.** Validated method parameters applied in the organic matter determination in natural water using a turbidimeter

Parameter of validation	Data
Analytical curve (n = 7) *	$y \pm 4.44 = (154.97 \pm 0.99 x) + (-2.44 \pm 0.19)$
R <sup>2</sup>	0.9998
Working range	0.41 mg-1.0 g OM L <sup>-1</sup>
Sensitivity	15.5
Limit of detection (LOD)	0.12 mg OM L <sup>-1</sup>
Limit of quantification (LOQ)	0.41 mg OM L <sup>-1</sup>
Recovery (%)	88.6%

\* Analytical curve was built following the formula  $y \pm S_y = (a \pm S_a x) + (b \pm S_b)$ . PARAMETERS:  $y$  is the turbidity (in NTU),  $x$  is the OM concentration (in mg L<sup>-1</sup>), and  $S$  values are the uncertainties ( $S_y$  and  $S_b$  in NTU;  $S_a$  in mg L<sup>-1</sup>).

applied in a semiquantitative data acquisition, instead of a quantitative application.

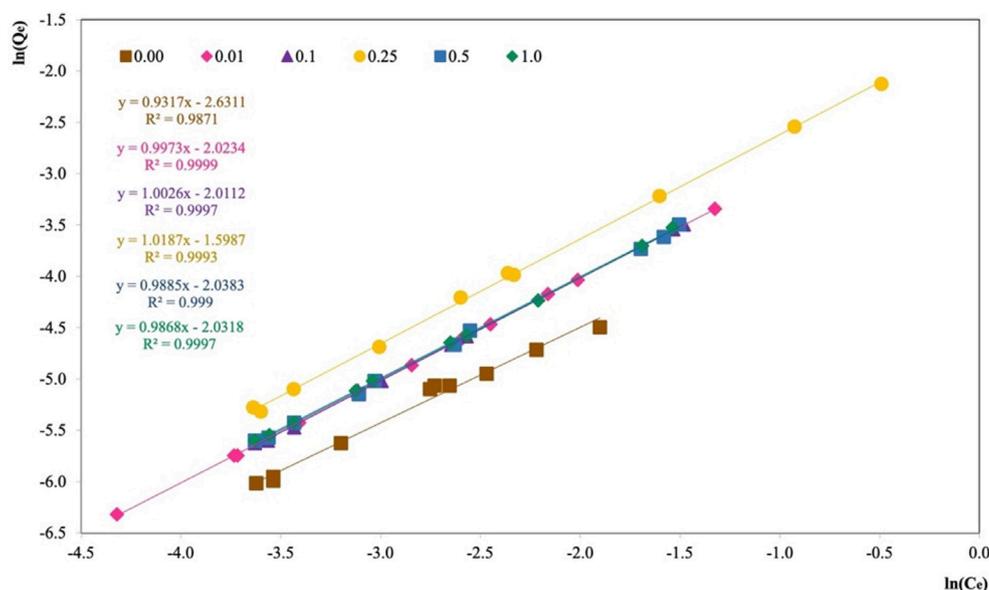
### 3.3. Adsorption processes

Evaluated under the perspective of the Environmental Physical-Chemistry, the use of *P. gounellei* was efficient in removing OM from the sample waters, and the results varied according to the type of sorbent (*in natura* and acid modified). In addition, the concentration of removed OM was proportional to the quantity of adsorbent. When the OM concentration was fixed in 0.5 mg L<sup>-1</sup>, the quantity removed proportional to the contact time. The maximum contact time was adjusted to be 48 h, due to economic issues, and the calculated curve supported sufficient data (as preliminary results) to carry out a study of the adsorption kinetics.

Thus, data of the remaining OM and the adsorbent concentration were plotted according to Langmuir and Freundlich adsorption models (Equation 3 and Equation 4). When compared the values of R<sup>2</sup> (via linear least squares

regression) (Table 3; Figure 1), Freundlich adsorption model was the most suited to the investigated adsorption process (R<sup>2</sup> ranging from 0.9871-0.9999 in Freundlich, against 0.0293-0.3419 in Langmuir; Table 3). Freundlich adsorption model considers the covering surface of the adsorbent material occurs in multilayer, with the formation of colloidal structures from the fixation of the OM on the adsorbent surface.<sup>24</sup>

Once the mathematical model of the adsorption isotherm was taken, the type of isotherm was also evaluated, according to Giles et al. (1960).<sup>33</sup> Thus, isotherm of type C (constant partition) was the best-fit line, in all samples. Type C isotherms are characterized by the process of constant partition between the concentration of the solute presents in the suspension and the number of adsorption sites, indicating a great affinity between the adsorbent (*P. gounellei*) and the adsorbate (OM). In addition, the linear form indicated how the number of adsorption sites remains constant during the adsorptive process; denoting that adsorption and desorption occur simultaneously until the establishment of the physical-



**Figure 1.** Freundlich adsorption isotherms for the OM removal using the *P. gounellei* acid-modified (0.001-1.0 mol HCl L<sup>-1</sup>) and *in natura* (0.0)

**Table 3.** Adsorptive parameters of the Freundlich and Langmuir isotherms calculated for the adsorption process for the removal of organic matter presents in natural water using the cactus *P. gounellei* (acid-modified and *in natura*)

Isotherms		[HCl] / mol L <sup>-1</sup>					
		0.00*	0.01	0.1	0.25	0.5	1.0
Freundlich	1/n	0.9291	0.9973	1.0026	1.0187	0.9885	0.9868
	$K_F / (\text{mg OM g}^{-1}) (\text{g mg}^{-1})^{1/n}$	$68.67 \times 10^{-3}$	$132.21 \times 10^{-3}$	$133.83 \times 10^{-3}$	$202.15 \times 10^{-3}$	$130.24 \times 10^{-3}$	$131.09 \times 10^{-3}$
	R <sup>2</sup>	0.9871	0.9999	0.9997	0.9993	0.9990	0.9997
Langmuir	$K_L / \text{g mg}^{-1}$	$47.11 \times 10^{-3}$	$6309.15 \times 10^{-3}$	$4480.28 \times 10^{-3}$	$2792.51 \times 10^{-3}$	$1328.90 \times 10^{-3}$	$1213.84 \times 10^{-3}$
	$Q_m / \text{mg OM g}^{-1}$	201.33	216.49	296.29	684.38	1,024.00	1,133.93
	R <sup>2</sup>	0.3419	0.0457	0.0293	0.1338	0.0831	0.2258

\* Sample and concentration 0.00 mol HCl L<sup>-1</sup> refer to the sample *in natura*, non acid-treated. ACRONYMS: 1/n Adsorption intensity;  $Q_m$  Maximum adsorption capacity;  $K_L$  Constants of Langmuir;  $K_F$  Constants of Freundlich; R<sup>2</sup> Coefficient of correlation.

chemical equilibrium. Regarding to the linearized Langmuir and Freundlich isotherms equations, linear parameters were calculated, and through the angular and linear coefficient, the parameters of adsorption (1/n and  $K_F$ ) were determined (Table 3).

The parameter 1/n (adsorption intensity) indicates if the adsorption is favorable or not (considering chemical characteristics of both, surface and adsorbate), where the value of  $n$  indicates the heterogeneity of the adsorbent surface. In addition, 1/n ranging between 1-10 represents the most favorable conditions for the adsorptive processing.<sup>19,34-36</sup> As presented in Table 3, all values of 1/n were observed close to 1 (ranging from 0.98 to 1.01), representing favorable adsorption conditions. In addition, samples of *P. gounellei* submitted to an acid treatment increased significantly their intensity of adsorption. Best result was obtained in the sample 0.25 mol HCl L<sup>-1</sup>, presenting a 1/n of 1.01, approximately 10% higher than in the sample *in natura*, which showed the smallest value of 1/n, 0.92 (Table 3). Thus, we consider that the acid treatment changed the adsorbent structure, probably increasing the amount of pores on the surface, besides changing the chemical structure, promoting a more intense adsorption and affecting the physical-chemical balance, intensifying the adsorption in relation to the desorption.

When analyzed the  $K_F$  constant (Table 3), all calculated values were higher in the samples treated with acid when compared to the *in natura*. Values calculated for 0.01, 0.1, 0.25, 0.5 and 1.0 mol HCl L<sup>-1</sup> were similar, presenting a  $K_F$  of  $\sim 132 \times 10^{-3}$  (mg OM g<sup>-1</sup>) (mg L<sup>-1</sup>)<sup>1/n</sup>. The most significant differences were observed in the sample *in natura*,  $K_F = 68.67 \times 10^{-3}$  (mg OM g<sup>-1</sup>) (mg L<sup>-1</sup>)<sup>1/n</sup>, and in the sample 0.25 mol HCl L<sup>-1</sup>,  $K_F = 202.15 \times 10^{-3}$  (mg OM g<sup>-1</sup>) (mg L<sup>-1</sup>)<sup>1/n</sup>, presenting 197% of difference.

Regarding the adsorption kinetics, at the final time (48 h), all the OM content was completely removed only in the samples 0.5 and 1.0 mol HCl L<sup>-1</sup>. Samples 0.00, 0.01, 0.1 and 0.25 removed 67, 65, 76, and 79% of OM, respectively (Table 4). Considering the adsorbed data concentration versus time, the results were plotted according to the mathematical models of pseudo-first order and pseudo-second kinetic orders. Following the linear coefficient of correlation (R<sup>2</sup>) (Table 4), the pseudo-

second kinetic order was the best-fit line, showing a R<sup>2</sup> ranging from 0.9887-0.9988 in pseudo-second order, versus 0.9326-0.9770 in pseudo-first order (Figure 2).

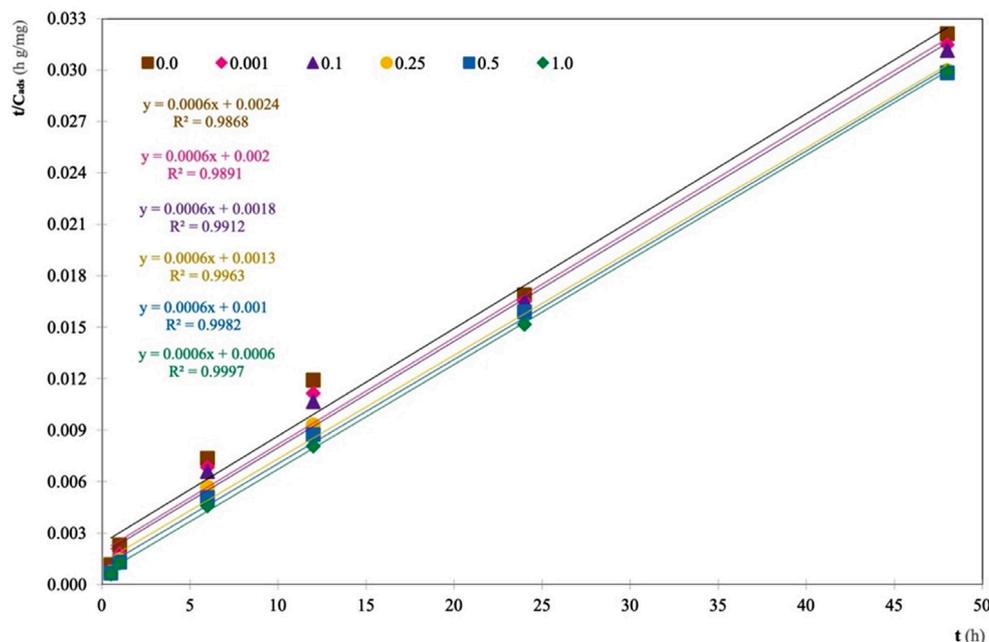
After determined the kinetic model of adsorption, the equations were linearized and, through the angular and linear coefficients, kinetic parameters ( $C_e$ ,  $C_{ads}$  and  $k_2$ ) were calculated. Values of  $C_e$  varied between 1.637 and 1.646 g OM g<sup>-1</sup> (gram of OM per gram of adsorbent). These values indicated that the adsorbent can adsorb 60% higher than the own weight (m/m), as expected, since the isotherm model indicates the multilayer formation, allowing successive adsorption until reaching equilibrium (Table 4).<sup>24,33-35</sup>

Comparing the values of  $C_e$ , *P. gounellei* acid-treated under soft conditions (0.01 and 0.1 mol HCl L<sup>-1</sup>) presented the highest equilibrium concentration ( $C_e = 1.683$  g OM g<sup>-1</sup>, Table 4). A high value of  $C_e$  indicates that the equilibrium is reached at higher concentrations of removing OM, which requires more time, during successive adsorption-desorption on the covering surface.<sup>25,34</sup> In addition, the smallest value was calculated in the sample *in natura*,  $C_e = 1,637$  g OM g<sup>-1</sup>.

Finally, considering the pseudo-second order rate constant, values of  $k_2$  (Table 4) were estimated using the linear coefficient of the pseudo-second order equation. Samples *in natura* and acid-treated under soft conditions (0.01 and 0.1 mol HCl L<sup>-1</sup>) presents a  $k_2$  around  $12 \times 10^{-5}$  L g<sup>-1</sup> h<sup>-1</sup>; samples treated at 0.25, 0.5 and 1.0 mol HCl L<sup>-1</sup> presented the following velocity constant:  $23 \times 10^{-5}$ ,  $32 \times 10^{-5}$  and  $49 \times 10^{-5}$  L g<sup>-1</sup> h<sup>-1</sup>, respectively. The best result was obtained in the sample treated with 1.0 mol HCl L<sup>-1</sup>, 282% higher than the sample *in natura*, reinforcing that the acid treatment was favorable to the adsorptive process in most of the analyzed attributes.

Once the velocity constant was determined, the relative velocities were calculated. Results varied depending on the amount of OM removed per unit of time, at a rate of  $k_2 \times d[\text{OM}]^2/dt$  (Table 5).

In relation to the acid-modified samples, those treated with more concentrated HCl presented higher velocities, resulting in a shorter removal time (Figure 3). For instance, sample 0.5 and 1.0 mol HCl L<sup>-1</sup> presented a  $v_1$  (velocity between 0.0 and 0.5 h) of  $16.8 \times 10^{-2}$  and  $18.0 \times 10^{-2}$  g OM h<sup>-1</sup> (gram of organic matter removed per hour), respectively;



**Figure 2.** Pseudo-second order adsorption kinetics for the OM removal using the *P. gounellei* acid-modified (0.001-1.0 mol HCl L<sup>-1</sup>) and *in natura* (0.0), at different contact times (0.5-48 h)

**Table 4.** Kinetic parameters of pseudo-first and pseudo-second order mathematical models for the adsorption process for the removal of organic matter presents in natural water using the cactus *P. gounellei* (acid-modified and *in natura*)

Kinetic model	Parameters	[HCl] / mol L <sup>-1</sup>					
		0.00*	0.01	0.1	0.25	0.5	1.0
Pseudo-first order	$C_e / \text{g OM g}^{-1}$	1.460	1.365	1.265	1.195	1.028	1.045
	$k_1 / \text{h}^{-1}$	$-118.079 \times 10^{-3}$	$-116.290 \times 10^{-3}$	$-106.445 \times 10^{-3}$	$-108.541 \times 10^{-3}$	$-104.142 \times 10^{-3}$	$-166.448 \times 10^{-3}$
	R <sup>2</sup>	0.9604	0.9690	0.9770	0.9720	0.9326	0.97254
Pseudo-second order	$C_e / \text{g OM g}^{-1}$	1.637	1.683	1.683	1.671	1.647	1.646
	$k_2 / \text{L g}^{-1} \text{h}^{-1}$	$12.9 \times 10^{-5}$	$12.6 \times 10^{-5}$	$12.6 \times 10^{-5}$	$23.7 \times 10^{-5}$	$32.0 \times 10^{-5}$	$49.4 \times 10^{-5}$
	R <sup>2</sup>	0.9868	0.9891	0.9912	0.9963	0.9982	0.9997

\* Sample and concentration 0.00 mol HCl L<sup>-1</sup> refer to the sample *in natura*, non-acid-treated. ACRONYMS:  $C_e$  Equilibrium concentration;  $k_1$  Pseudo-first order rate constant;  $k_2$  Pseudo-second order rate constant; R<sup>2</sup> Coefficient of correlation

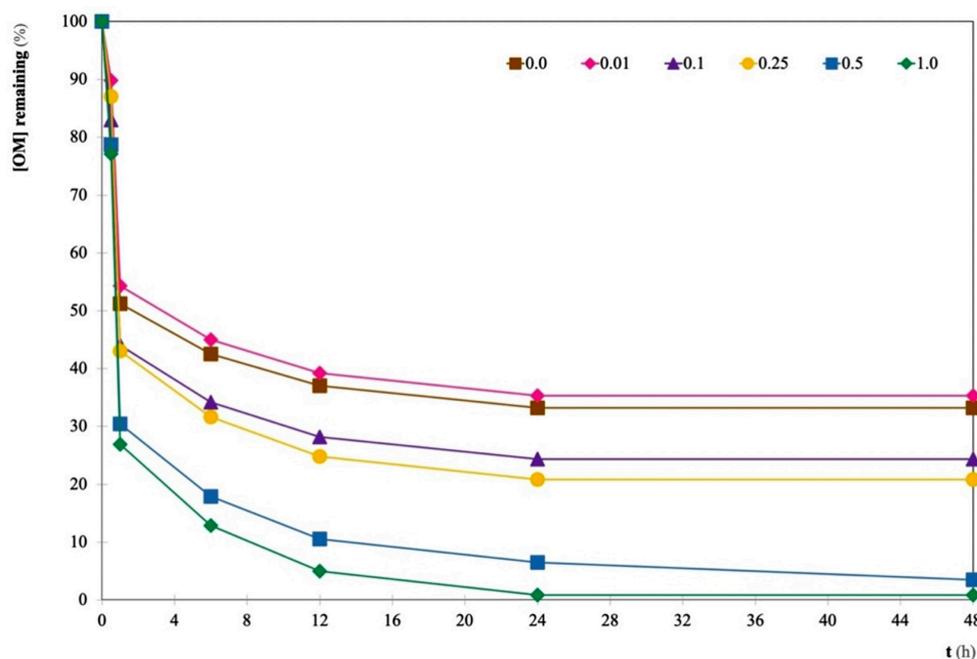
and  $v_2$  (velocity between 0.5 and 1.0 h) of  $21.3 \times 10^{-2}$  and  $22.8 \times 10^{-2}$  g OM h<sup>-1</sup>. Considering the quantity treated at the first hour, ~70% of all OM were removed. In the other samples, these quantities were quantified around ~40-50%, and the velocities varied between 0.08-0.592 g OM h<sup>-1</sup>.

In addition, sample *in natura* presented the same velocity observed in the sample 0.5 mol HCl L<sup>-1</sup> ( $16.8 \times 10^{-2}$  g OM h<sup>-1</sup>), however,  $v_2$  between both samples were different in 126% ( $21.6 \times 10^{-2}$  in sample *in natura* and  $38.0 \times 10^{-2}$  g OM h<sup>-1</sup> in sample 0.5 mol HCl L<sup>-1</sup>; Table 5).

**Table 5.** Velocity of OM removal in function of the time ( $v = -k_2 \times d[\text{OM}]^2/dt$ ) using the cactus *P. gounellei* (acid-modified and *in natura*)

Sample (mol HCl L <sup>-1</sup> )	$-k_2 \times d[\text{OM}]^2/dt$ (g OM h <sup>-1</sup> ) *					
	0-0.5 h	0.5-1 h	1-6 h	6-12 h	12-24 h	24-48 h
0.00**	16.8	26.4	3.9	1.7	1.7	0.1
0.01	8.0	48.0	3.2	1.8	1.5	0.1
0.1	13.4	48.0	3.2	1.7	1.3	0.2
0.25	10.2	59.2	3.8	1.8	0.9	0.1
0.5	16.8	59.2	4.3	1.7	0.6	0.1
1.0	18.0	61.2	5.3	1.4	0.4	0.0

\* [OM] refers to the concentration of removed OM; values on scale  $\times 10^{-2}$ . \*\* Sample and concentration 0.00 mol HCl L<sup>-1</sup> refer to the sample *in natura*, non-acid-treated



**Figure 3.** Remaining [OM] monitored during the adsorptive process using the cactus *P. gounellei* acid-modified and *in natura* at different times of adsorption (0-48 h)

Based on this result, it is possible to consider that sample *in natura* initially had the same quantity of adsorption sites present in the samples treated with HCl in soft conditions. However, sites saturation occurred in the first minutes of adsorption, removing approximately 21% of the OM in solution, decreasing in the next calculated velocities. Statistical differences evidenced that higher acid concentrations led to a production of a material of higher efficiency and potential to be applied in the treatment of natural water bodies rich in organic matter, in special those used as drinking fountain in animal creations/ livestock activity.

#### 4. Conclusion

The present study confirms that it is possible to remove the OM present in natural water using the *P. gounellei* as an alternative adsorbent, intending the good practices in livestock and animal welfare. Isotherm of Freundlich (type C) and kinetics of pseudo-second order were the best-fit in the elucidation of the adsorptive processes. Samples of natural waters are significantly clear of OM (93-99% of removal) using samples treated with 0.5 and 1.0 mol HCl L<sup>-1</sup>. In a future perspective, we propose to scale-up the technology and treat larger volumes of natural waters, in addition to evaluating the effect on animal welfare.

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#### References

- Hocquette, J.-F.; Botreau, R.; Picard, B.; Jacquet, A.; Pethick, D. W.; Scollan, N. D.; Opportunities for predicting and manipulating beef quality. *Meat Science* **2012**, *92*, 197. [Crossref]
- Sinclair, M.; Zito, S.; Phillips, C.; The Impact of Stakeholders' Roles within the Livestock Industry on Their Attitudes to Livestock Welfare in Southeast and East Asia. *Animals* **2017**, *7*, 6. [Crossref]
- Sundrum, A.; Organic livestock farming. *Livestock Production Science* **2001**, *67*, 207. [Crossref]
- Lehikoinen, E.; Parviainen, T.; Helenius, J.; Jalava, M.; Salonen, A.; Kumm, M.; Cattle Production for Exports in Water-Abundant Areas: The Case of Finland. *Sustainability* **2019**, *11*, 1075. [Crossref]
- Nardone, A.; Ronchi, B.; Lacetera, N.; Ranieri, M. S.; Bernabucci, U.; Effects of climate changes on animal production and sustainability of livestock systems. *Livestock Science* **2010**, *130*, 57. [Crossref]
- Thornton, P. K.; van de Steeg, J.; Notenbaert, A.; Herrero, M.; The impacts of climate change on livestock and livestock systems in developing countries: A review of what we know and what we need to know. *Agricultural Systems* **2009**, *101*, 113. [Crossref]
- Matilainen, A.; Vepsäläinen, M.; Sillanpää, M.; Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science* **2010**, *159*, 189. [Crossref]

8. Nibert, D.; *Animal oppression and capitalism* Praeger: Westport, 2017.
9. Stucki, S.; Beyond Animal Warfare Law: Humanizing the “War on Animals” and the Need for Complementary Animal Rights. *SSRN Electronic Journal* **2021**, 1. [[Crossref](#)]
10. Bakhshi, F.; Najdegerami, E. H.; Manaffar, R.; Tukmechi, A.; Farah, K. R.; Use of different carbon sources for the biofloc system during the grow-out culture of common carp (*Cyprinus carpio* L.) fingerlings. *Aquaculture* **2018**, *484*, 259. [[Crossref](#)]
11. Duan, H.; Ma, R.; Loiselle, S. A.; Shen, Q.; Yin, H.; Zhang, Y.; Optical characterization of black water blooms in eutrophic waters. *Science of The Total Environment* **2014**, *482–483*, 174. [[Crossref](#)]
12. Musadji, N. Y.; Lemée, L.; Caner, L.; Porel, G.; Poinot, P.; Geffroy-Rodier, C.; Spectral characteristics of soil dissolved organic matter: Long-term effects of exogenous organic matter on soil organic matter and spatial-temporal changes. *Chemosphere* **2020**, *240*, 1. [[Crossref](#)] [[PubMed](#)]
13. Umar, S.; Munir, M. T.; Azeem, T.; Ali S.; Umar, W.; Rehman, A.; Shah, M. A.; Effects of water quality on productivity and performance of livestock: a mini review. *Veterinaria* **2014**, *2*, 11. [[Link](#)]
14. Oliveira, E. G.; Santos, F. J. S.; *Piscicultura e os desafios de produzir em regiões com escassez de água* Embrapa Meio-Norte: Teresina, 2015.
15. Sillanpää, M.; Ncibi, M. C.; Matilainen, A.; Vepsäläinen, M.; Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review. *Chemosphere* **2018**, *190*, 54. [[Crossref](#)]
16. Mohtashami, R.; Shang, J. Q.; Treatment of automotive paint wastewater in continuous-flow electroflotation reactor. *Journal of Cleaner Production* **2019**, *218*, 335. [[Crossref](#)]
17. Paulista, L. O.; Presumido, P. H.; Theodoro, J. D. P.; Pinheiro, A. L. N.; Efficiency analysis of the electrocoagulation and electroflotation treatment of poultry slaughterhouse wastewater using aluminum and graphite anodes. *Environmental Science and Pollution Research* **2018**, *25*, 19790. [[Crossref](#)]
18. Xu, Y.; Nakajima, T.; Ohki, A.; Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasuzelite. *Journal of Hazardous Materials* **2002**, *92*, 275. [[Crossref](#)]
19. Hsu, T. C.; Experimental assessment of adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> from aqueous solution by oyster shell powder. *Journal of Hazardous Materials* **2009**, *171*, 995. [[Crossref](#)]
20. Rubio, F.; Gonçalves, A. C.; Meneghel, A. P.; Tarley, C. R. T.; Schwantes, D.; Coelho, G. F.; Removal of cadmium from water using by-product *Crambe abyssinica* Hochst seeds as biosorbent material. *Water Science and Technology* **2013**, *68*, 227. [[Crossref](#)]
21. Santos, M. V. F.; Lira, M. A.; Dubeux Junior, J. C. B.; Guim, A.; Mello, A. C. L.; Cunha, M. V.; Potential of Caatinga forage plants in ruminant feeding. *Revista Brasileira de Zootecnia* **2010**, *39*, 204. [[Crossref](#)]
22. Nascimento, V. T.; Moura, N. P.; Silva Vasconcelos, M. A.; Maciel, M. I. S.; Albuquerque, U. P.; Chemical characterization of native wild plants of dry seasonal forests of the semi-arid region of northeastern Brazil. *Food Research International* **2011**, *44*, 2112. [[Crossref](#)]
23. Langmuir, I.; The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* **1918**, *40*, 1361. [[Crossref](#)]
24. Freundlich, H.; Über die Adsorption in Lösungen. *Zeitschrift für Physikalische Chemie* **1907**, *57U*, 385. [[Crossref](#)]
25. Ho, Y. S.; McKay, G.; A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection* **1998**, *76*, 332. [[Crossref](#)]
26. CETESB; *Guia nacional de coleta e preservação de amostras: água, sedimento, comunidades aquáticas e efluentes líquidos*. ANA: Brasília, 2011.
27. Eurachem Europe *Eurachem Guide* Eurachem Guide: London, 2019.
28. ISO; *General requirements for the competence of testing and calibration laboratories* ISO: Geneva, 2005.
29. UN-WHO; *Good Laboratory Practice (GLP)* WHO Library Cataloguing-in-Publication Data: Geneva, 2008.
30. Omar, A. F.; MatJafri, M. Z.; Turbidimeter design and analysis: a review on optical fiber sensors for the measurement of water turbidity. *Sensors* **2009**, *9*, 8311. [[Crossref](#)]
31. Zhu, Y.; Marchuk, A.; Bennett, J. M.; Rapid method for assessment of soil structural stability by turbidimeter. *Soil Science Society of America Journal* **2016**, *80*, 1629. [[Crossref](#)]
32. Thurman, E. M.; *Organic Geochemistry of Natural Waters* Springer Netherlands: Dordrecht, 1985.
33. Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society (Resumed)* **1960**, 3973. [[Crossref](#)]
34. Mittal, A.; Kurup, L.; Mittal, J.; Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers. *Journal of Hazardous Materials* **2007**, *146*, 243. [[Crossref](#)]
35. Nuhnen, A.; Janiak, C.; A practical guide to calculate the isosteric heat/enthalpy of adsorption via adsorption isotherms in metal-organic frameworks, MOFs. *Dalton Transactions* **2020**, *49*, 10295. [[Crossref](#)]
36. Muhammad, J.; Din, I.; Defluoridation of water using *Dodonaea viscosa* leaf powder: a study of adsorption isotherms. *Fluoride* **2020**, *53*, 90. [[Link](#)]